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THE NATURE AND PROPERTIES OF CORN OIL.

II. DETERMINATION OF THE CONSTITUTION.

BY HERMANN T. VULTÉ AND HARRIET WINFIELD GIBSON.

IN the present investigation an attempt has been made to iden-
tify, so far as possible, the series of fatty acids contained in
maize oil. Although a complete separation has not been effected,
owing to the difficulty of isolating these acids and to the imper-
fect knowledge we have of their properties, it has been found
practicable to determine the principal acids found in the oil,
including three never before reported, and to definitely settle the
relationship existing between maize oil and other oils possessing
somewhat similar properties.

The oil of maize is a fixed seed oil, composed of a highly com-
plex mixture of glycerides of the fatty acids, together with a
small proportion of some volatile oil and a rather large percentage
of unsaponifiable matter.

CONSTITUENTS OTHER THAN FATTY ACIDS.

The question of the nature of the volatile oil peculiar to corn
oil has not been considered in the present article. Its existence
has been recognized by nearly all observers, and it is to this

cause that the characteristic grain-like odor and taste of the oil are due.

The unsaponifiable matter is very largely phytosterol or phytosteryl alcohol. The amount present, as determined by the process of Foster and Reichelmann, is found to be 1.41 per cent., a rather large amount in comparison with that in most seed oils. To the presence of phytosterol is due one of the most characteristic tests for maize oil ; *i. e.*, a fine violet coloration when one drop of concentrated sulphuric acid is added to a carbon disulphide solution of the oil and the mixture is allowed to stand for twenty-four hours.

A small amount of lecithin is also present in the unsaponifiable matter. The method of Benedikt and Lewkowitsch was employed for this determination and the amount of phosphorus pentoxide recovered was 0.98 per cent. From this, the calculated amount of lecithin present in maize oil is 1.11 per cent., making the total amount of unsaponifiable matter 2.52 per cent.

The percentage of glycerol, as determined by Hehner's dichromate method, is somewhat high, running from 10.35 to 10.55 per cent.

INSOLUBLE FATTY ACIDS.

The mixed insoluble fatty acids were prepared in considerable bulk, for analysis, by a process analogous to that used in determining the Reichert value, except that no attempt was made to have the work quantitative. The oil was saponified by aqueous potassium hydroxide in considerable excess, the soap decomposed by dilute sulphuric acid, and the resultant liquid heated until the oily layer of liberated fatty acids became clear and transparent. The whole mass was then transferred to a separating funnel, the aqueous layer drawn off, and the fatty acids washed with boiling water until the wash-water was neutral to litmus. The insoluble acids were then subjected to a steam distillation at the ordinary pressure and the residue washed with boiling water, filtered through a dry filter, and dried at 100° C. Considerable difficulty was found in obtaining uniform samples for analysis, owing to the sharp separation of the acids into a solid and a liquid portion.

The ordinary constants of the mixed insoluble acids, prepared as above, were first determined, the melting-point being estab-

'lished by the method of La Sueur and Crossley[1] and the saponification value both by titration and by the Koettstorfer method. A tabulation of the results obtained follows :

Sp. gr. at 100° C.................................... 0.8529
Melting-point .... 22.4° C.
Iodine absorption.................................. 120.98
Bromine thermal value............................. 21.6° C.

SAPONIFICATION VALUE.

By titration 198.29
By Koettstorfer.................................... 200.01

MEAN COMBINING WEIGHT.

By titration....................................... 282.98
By Koettstorfer.................................... 280.64

In connection with these results a statement is given of the figures obtained by other observers, as follows :

COMPARISON WITH RESULTS OF OTHER OBSERVERS.

MELTING-POINT.

Melting-point acids.	Observers.	References.
10.5°–12.2° C.	Hoppe-Seyler[2]	Bull. Soc. Chim. (1866),[2], 6, 342.
16°–18° C.	Dulière	J. Pharm. (1897), 217.
18°–20° C.	DeNegri and Fabris	Ztschr. anal. Chem., 33, 547.
20° C.	Jean	J. Soc. Chem. Ind., 11, 504.
39.5° C.	DeNegri[3]	Chem. Ztg., 22, 961–976.

IODINE ABSORPTION.

Hübl No. acids.	Observer.	Reference.
113–115	De Negri and Fabris	Ztschr. anal. Chem., 33, 547.
123.27	De Negri[3]	Chem. Ztg., 22, 961.
125	Spüller[2]	Dingl., 264, 626.
126.4	Hopkins	J. Am. Chem. Soc., Dec., 1898.

SAPONIFICATION VALUE.

Sapon. value.	Mean. mol. wt.	Observer.	Reference.
198.4	282.76	Hart	Chem. Ztg., 6, 1522.

An attempt was next made to obtain an approximate idea of the relative amounts of liquid and of solid fatty acids present in the mixture and, for this purpose, the method proposed by Muter and De Koningh[4] was employed. The results obtained must not be regarded as entirely accurate, since the lead salts of the acetic

[1] *J. Soc. Chem. Ind.*, Nov. 30, 1898.
[2] Ether extract.
[3] Petroleum ether extract.
[4] Allen : "Commercial Organic Analysis," Vol. II(I), 247.

series of fatty acids are not wholly insoluble in ether and those of the oleic and the linolic series are not completely soluble. The constants of the two fractions were then determined, great care being taken to avoid oxidation during the process, and a tabulation of the results obtained follows :

	Percentage.	Iodine absorption.	Molecular weight.	Koettstorfer figure.
Liquid fatty acids	72.26	135.97	284.45	197.22
Solid fatty acids	27.74(calc.)	54.23	269.78	207.94

Wallenstein and Finck report an iodine absorption figure of 140.7 for the liquid fatty acids of this oil, a somewhat higher figure than has been obtained in the present investigation.

It will be noticed that the percentage of liquid fatty acids is high. The terms " liquid" and " solid" used in this connection are misleading since, as will be shown later, one of the principal acids of maize oil is both solid and unsaturated, having its lead salt soluble in ether.

FRACTIONAL PRECIPITATION OF MIXED ACIDS.

Forty grams of the mixed insoluble fatty acids were dissolved in hot neutral alcohol, care being taken to use enough alcohol to insure complete solution at all temperatures. To the hot liquid was added a boiling solution of 1.5 grams magnesium acetate in alcohol and the mixture was then thoroughly agitated and allowed to stand for twenty-four hours. As no precipitate was thrown down, the operation was repeated with a second portion of magnesium acetate and, upon standing, a white solid, like the scrapings of candles, separated out. This precipitate was filtered off and a fresh portion of magnesium acetate added to the filtrate as before, the operation being repeated as long as it was possible to obtain new precipitates. In this manner four successive fractions were separated, all white and all but the first curdy in appearance. The fifth fraction was obtained by making the liquid strongly alkaline with ammonia, before the addition of fresh magnesium acetate, and allowing the mixture to stand for three days before filtering. The sixth and seventh fractions were obtained by neutralizing the liquid with acetic acid and then treating it with lead acetate. The precipitate thus obtained was filtered off, dissolved in ether as far as possible, and the insoluble portion fil-

tered out. The final fraction, having its lead salt soluble in ether, was then freed from the ether by gently heating the liquid.

The several fractions were next well washed with cold dilute alcohol, dried in filter-paper, and decomposed by hot, dilute hydrochloric acid. The liberated fatty acids were then washed with boiling water until neutral to methyl orange, filtered and dried as in the Hehner and Angell process. The purified acids were now examined for melting-point, iodine absorption, bromine absorption, saponification figure, and mean molecular weight.

In the determination of melting-point, a short piece of glass tubing with small bore was coated over one end with a film of the acid and bound to the bulb of a delicate thermometer. This was immersed in water, which was gradually raised in temperature. The point at which the fatty film was detached from the tube and rose to the surface was recorded as the melting-point.

A tabulation of the results obtained follows, and it will be observed that the acids constituting the several fractions give a pretty regular series of values for all constants determined.

APPEARANCE OF THE SEVERAL FRACTIONS.

1. White waxy mass like the scrapings of candles.
2. White warty substance like soft tallow.
3. Pale yellow solid, rather harder than butter.
4. Buttery, dark brown mass. The magnesium salt of this fraction was very stable and, upon being decomposed by acid, immediately oxidized to a dark brown color. The filtrate was colored bright yellow and had a peculiar odor, showing that some decomposition-product had been formed.
5. Similar to 4, but somewhat softer.
6. Similar to 1.
7. Dark red-brown liquid, of comparatively low viscosity.

	Melting-point.	Mean mol. weight.	Saponification value.	Iodine absorption.	Bromine absorption.	Equivalent iodine absorption.
1	50.2	272.00	206.25	15.35	....	....
2	37.2	276.03	203.24	69.74	....	....
3	35.8	284.76	197.00	101.94	64.55	102.46
4	31.1	289.75	193.62	102.77	66.23	105.14
5	21.5	287.60	195.06	114.98	73.22	116.26
6	55.2	268.11	209.24	9.51	5.32	8.45
7	Liquid	286.07	196.11	137.61	85.91	136.39

An examination of the several fractions and of their constants,

as given in the foregoing table, indicates the presence, particularly in the fourth fraction, of some unsaturated fatty acid which is readily oxidizable in the air. The melting-point and iodine absorption of this fraction suggest hypogaeic acid, and an ultimate analysis of the substance, twice repeated, gave a formula very nearly corresponding to $C_{16}H_{30}O_2.2H_2O$, except that the percentage of oxygen was somewhat high. The presence of water, due to the impossibility of completely drying so oxidizable an acid, explains the high molecular weight of this fraction and the excess of oxygen is, of course, due to the oxidizability of the oil. From the foregoing evidence the presence of hypogaeic acid as a characteristic acid of maize oil may be considered as conclusively proved.

A separate investigation, in the method suggested by Renard,[1] was conducted to determine the presence of arachidic acid. A small crop of crystals was obtained, showing the characteristic form of arachidic acid under the microscope, but the quantity recovered was too small for further investigation.

The occurrence of stearic, palmitic, and oleic acids in maize oil was first reported by Hoppe-Seyler[2] in 1866. He succeeded in isolating these acids, and their presence has since been confirmed by many observers. Linolic acid was first determined in 1894 by Rokitiansky,[3] who prepared its oxidation-product, sativic or tetrahydroxystearic acid. This result is confirmed by a late observer, C. G. Hopkins,[4] of Cornell University, who finds a large percentage of linolic acid in corn oil. Rokitiansky also asserts the presence of a hydroxylated acid (probably ricinoleic) in the solid fatty acids, and this conclusion is rendered probable by the somewhat high acetyl figure (11.12–11.49) of the oil.

A summary of the insoluble fatty acids shown to exist in the oil of maize is therefore as follows :

Name of acid.	Formula.	Name of analyst.
Stearic	$C_{18}H_{36}O_2$	Hoppe-Seyler
Palmitic	$C_{16}H_{32}O_2$	Hoppe-Seyler
Arachidic	$C_{20}H_{40}O_2$	Vulté and Gibson
Hypogaeic	$C_{16}H_{30}O_2$	Vulté and Gibson
Oleic	$C_{18}H_{34}O_2$	Hoppe-Seyler
Linolic	$C_{18}H_{32}O_2$	Rokitiansky
Ricinoleic(?)	$C_{18}H_{34}O_3$	Rokitiansky

[1] Allen : "Commercial Organic Analysis," II (I), 134.
[2] Bull. Soc. Chim. (1866), [2], 6, 342.
[3] Ph. Russ. (1894), 712–713.
[4] This Journal, 20, 948.

SOLUBLE FATTY ACIDS.

In the determination of the constants of maize oil, the Reichert value (4.2–4.3) obtained as the result of a large number of tests was found to be higher than that of any other seed oil, cocoanut oil (3.5–3.7) coming next. The figures obtained for this constant by other analysts differ widely in value, running from 0.0[1] to 6.7.[2] The Reichert value and high percentage of glycerine indicate the presence of a notable amount of volatile acids and, as comparatively little attention has been paid to their determination, certain observers going so far as to doubt their existence, it was thought well to attempt their identification, so far as possible. For this purpose the mixed acids were prepared as in the Hehner and Angell process, and the insoluble acids filtered off. An aliquot portion of the filtrate was then neutralized with decinormal potassium hydroxide, methyl orange indicator and the titration continued until neutral to phenolphthalein. The excess of decinormal potassium hydroxide of course represents the soluble fatty acids. (It was found that 1 gram of the oil required 0.0088 gram potassium hydroxide for the neutralization of its volatile acids, this corresponding to a Reichert value of 3.9 and a mean molecular weight of about 130.)

The larger part of the filtrate was then saturated with calcium chloride and allowed to stand. A small amount of oil separated out, showing the presence of acids higher than formic and acetic but lower in the series than lauric. No attempt was made. to identify the acids in this fraction, but Rokitiansky reports the probable presence of caproic, caprylic, and capric acids.

A portion of the aqueous liquid was carefully separated from all oily drops and heated with alcohol and concentrated sulphuric acid. The fragrant and characteristic odor of ethyl acetate was produced in a marked degree, thus establishing the presence of acetic acid, an acid never before reported for maize oil. As a confirmatory test, ferric nitrate was added drop by drop to a portion of the original filtrate. The blood-red color characteristic of ferric acetate was obtained and responded to the usual tests for establishing its identity.

Another portion of the original filtrate was treated with silver

[1] Hopkins.
[2] Morse: N. H. Expt. Sta. Bull. (1892), 16, 19.

nitrate and gently warmed. A marked precipitate of metallic silver was formed, this proving the presence of formic acid in corn oil. This acid was reported by Rokitiansky, but its occurrence has not been confirmed by any later observer.

The soluble acids thus far determined in corn oil are therefore summarized as follows :

Name of acid.	Formula.	Name of analyst.
Formic	CH_2O_2	Rokitiansky
Acetic	$C_2H_4O_2$	Vulté and Gibson
Caproic[1]	$C_6H_{12}O_2$	Rokitiansky
Caprylic[1]	$C_8H_{16}O_2$	Rokitiansky
Capric[1]	$C_{10}H_{20}O_2$	Rokitiansky

Scientific knowledge as to the properties of the various fatty acids is at present so scanty and fragmentary and the lack of any connected scheme for their analysis is so absolute that the complete investigation of any oil presents almost insurmountable difficulties. Further examination of corn oil is needed in order to establish or disprove the presence of caproic, caprylic, capric, and ricinoleic acids and also to determine the relative percentages of the various acids with accuracy. The present investigation adds to the known constituents of the oil, acetic, hypogaeic, and arachidic acids, and confirms the presence of formic acid, which was up to this time considered doubtful.

KILGORE'S MODIFICATION OF THE VOLUMETRIC METHOD OF ESTIMATING PHOSPHORIC ACID.[2]

BY C. B. WILLIAMS.

IN the laboratories of fertilizer control stations and other institutions where a large number of determinations of phosphoric acid are required to be made quickly and accurately each year, it has been recognized for some time as almost imperative that some method shorter than the "gravimetric" should be devised. In 1894 Mr. Kilgore, then reporter on phosphoric acid for the Association of Official Agricultural Chemists, realizing this

[1] Probable only.
[2] Read before the November meeting of the North Carolina Section of the American Chemical Society.

urgent demand, was the first to take up systematically the task by first thoroughly investigating himself and then submitting, as reporter, to the test of the Association the modified volumetric method. In his report he gave credit to Mr. Henry Pemberton who had, the previous year, published the description of a method based on this principle and which had been used very satisfactorily by a number of chemists. With this latter method, Mr. Kilgore had obtained fairly good but not uniformly good results.

After considerable experimentation as regards precipitant, precipitation, and filtration, he proposed a modification of this method, stating he had found that the modification gave him more satisfactory results with fertilizers. Since then each successive year has witnessed a still further modification until now we have a method that is used in a large number of laboratories in America with very gratifying results both in point of accuracy and rapidity.

The writer was, during the past spring, enabled to precipitate by shaking, wash and titrate thirty phosphoric acid samples daily with great facility by the modified volumetric method.

The reagents used are the same as those prescribed for the volumetric method by the Association of Official Agricultural Chemists except that the strengths of the standard solutions of ●potassium hydroxide[1] and nitric acid are made up so that 1 cc. of each will represent 0.5 milligram of phosphoric acid, this being one-half the strength given in the Association method.

The method as carried out is as follows :

Totals are brought in solution in the usual way by boiling in a 200 cc. flask, on a sand-bath, 2 grams fertilizer with 30 cc. concentrated nitric acid and 10 cc. concentrated hydrochloric acid to about 8 or 10 cc. concentration, except in fertilizers containing much iron and alumina, in which instance 30 cc. concentrated hydrochloric acid alone is first added and boiled for about thirty or forty minutes ; then, after slightly cooling, 30 cc. concentrated nitric acid is added and the boiling continued until the excess of hydrochloric acid is removed. After cooling make up to volume and filter out aliquot portions or allow to stand several hours before

[1] The standard potassium hydroxide is freed from carbon dioxide by first dissolving it in 95 per cent. alcohol, letting settle and then filtering off by reverse filtration the supernatant solution free from the insoluble potassium carbonate. This method is much quicker and simpler than the barium hydroxide method.

measuring out.   This latter is done in order that the supernatant
liquid may become perfectly clear so it can be measured out with
a pipette without filtration.

Twenty cc. of solution corresponding to 0.2 gram fertilizer
(except in samples containing over 20 per cent. of phosphoric
acid, when 10 cc. is used) are measured into a 500 cc. Erlenmeyer
flask, the inside diameter of whose neck measures about 40 mm.,
and to it is added 10 to 12 grams of ammonium nitrate and 50 cc.
of distilled water.   Neutralize the excess of acid with ammonia.
When the contents have cooled, 30 cc. of recently filtered molybdic
solution are added and the flask, after securely stoppering with
a rubber stopper, is placed in a Wagner shaking machine which is
revolved by a hot air motor and here shaken for thirty minutes.
The shaking machine is maintained at 45 to 55 revolutions per
minute, as this velocity has been found to give the maximum
agitating efficiency.   Remove the flask from the shaking machine
and filter and wash by suction on a filter prepared as follows :

Through the rubber stopper in a 16-ounce pressure bottle of
Erlenmeyer form is passed the small end of a carbon filter; in the
bottom of this is a perforated porcelain plate or disk to which is
rigidly fastened a No. 19 copper wire, about 25 cm. long, that
projects downwards into the pressure bottle.   The disk is
covered with a thin layer of asbestos.

After thoroughly transferring the ammonium phosphomolyb-
date and washing out the flask onto the asbestos filter, six more
washings are given the precipitate.   Then remove the stopper
from the pressure flask with the small end of the carbon filter still
stuck through it and hold upright over the sink and wash the
outside free from acid with distilled water.   Reverse the carbon
filter into the mouth of the flask that originally contained the
precipitate, still holding the small stem, and by means of the
copper wire that extends beyond the small end of the carbon
filter, push out the disk, asbestos and precipitate into the flask ;
wash the disk and inside of carbon filter carefully and titrate,
using a stirring rod about 30 cm. long to thoroughly agitate dur-
ing the operation.

In determining insolubles, 40 cc. of solution, corresponding to
0.4 gram fertilizer, are taken.   The precipitation, shaking,
washing, and titrating are practically the same as with totals,

except that little or no water is added in preparing for precipitation. During the past spring 1,000 totals and 1,000 insolubles were made by the above method with not a single incomplete precipitation, the yellow precipitate always coming down in a granular form that was easily filtered and washed.

Distilled water must be used in washing, as the suspended matter in ordinary water, in case it contains any, will not only retard filtration, but will form a compact coating over the precipitate that will greatly increase the difficulty of effecting a solution of the yellow precipitate with standard alkali as well as obscuring the color change of the indicator.

During the past year a large number of comparative results have been obtained in this laboratory on commercial fertilizers offered for sale in the State to test the volumetric method, as described above, with the regular official gravimetric method of the Association. In all instances results were extremely satisfactory.

During the past summer, three samples (two of ground phosphate rock and one of American slag) sent out by the referee on phosphoric acid for the Association of Official Agricultural Chemists, were analyzed with the following results:

No.	Gravimetric method.	Volumetric method.
		13.45
389[1]	$\begin{cases} 13.55 \\ 13.43 \end{cases}$	13.50
		13.51
		13.50
	$\begin{cases} 17.21 \\ 17.23 \end{cases}$	16.88
		16.93
390[2]	$\begin{cases} 17.27 \\ 17.35 \end{cases}$	16.95
		16.90
	$\begin{cases} 17.33 \\ 17.27 \end{cases}$	
	$\begin{cases} 26.01 \\ 26.10 \end{cases}$	25.90
391[1]		25.80
	$\begin{cases} 26.11 \\ 26.02 \end{cases}$	25.85
		25.88

It will be noticed that the gravimetric results on sample No. 390 are perceptibly higher than those determined volumetrically. This is probably due to the presence of iron in the mag-

[1] Ground phosphate rock.
[2] American slag.

nesium pyrophosphate as a qualitative test, for iron revealed
its presence there.   As sample No. 391 contains 4.70 per cent.
ferric oxide, this may account for the wider variation than in
No. 389 between the gravimetric and volumetric results.

RALEIGH, N. C.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF LAFAYETTE
COLLEGE.]

A METHOD FOR PREPARING NORMAL, SEMINORMAL, DECINORMAL, ETC., SULPHURIC ACID OF EXACT STRENGTH.

BY RICHARD K. MEADE.

Received November 10, 1900.

THE principal beauty of the normal system in volumetric
analysis is the doing away with calculations.   If then it is
necessary to use a factor for converting to normal with a solution
much of the usefulness of the system is destroyed.   Unfortunately
with by far the larger number of reagents used in volumetric
analysis it is only with the greatest care that such solutions can
be made of normal strength.   Of the commonly used acid and
alkali solutions, only oxalic acid and sodium carbonate can be
prepared of exact strength, without first having another standard
solution against which to balance a preliminary and then the
exact solution.   Even then, the latter is frequently too wide of
the normal value to be used without a factor.   The writer has
been for some time preparing normal, seminormal, and more par-
ticularly decinormal sulphuric acid of exact strength by the method
given below.   The solution as prepared by this method needs no
checking, except as a safeguard against errors of manipulation
on the part of the analyst.

If the electric current is passed through a solution of copper
sulphate the salt is decomposed, copper separating upon the cathode
and sulphuric acid at the anode.   This latter remains in solution
and is not decomposed by the current.   Hart and Croasdale[1]
took advantage of this reaction to standardize alkali solutions.
Their results were highly accurate.   The writer has frequently
made use of this method of standardizing alkali and has
obtained results far more satisfactory than by any other method.

[1] J. Anal. Chem., 4, 424.

The method of preparing tenth-normal sulphuric acid by means of this reaction is as follows :

12.487 grams of pure crystallized copper sulphate are dissolved in about 750 cc. of distilled water in a lipped beaker capable of holding about a liter. Into this solution, after cooling, is introduced a cylinder of copper foil attached to the minus (—) wire of an electric circuit. This copper cylinder may be made from 0.015 inch copper foil. The foil is cut the required length (three times the diameter of the beaker + one-half inch) curled so that the ends lap, and holes punched through the two thicknesses of foil with a sharp nail. Wire is then run through the holes, fastening the two ends of the foil together. A platinum rod for an anode is next passed through a perforated watch-glass covering the beaker into the copper sulphate solution. A current of electricity of from one to one and a half amperes is now passed through the solution for about eight hours ; or all night if the decomposition is begun in the afternoon. In the morning the watch-glass is removed and rinsed off together with the cylinder and the rod into the beaker. The solution is then transferred to a liter graduated flask ; any copper which may have dropped off the cylinder into the beaker is to be washed well by decantation, rinsing the beaker at the same time into the flask. The contents of the latter are then diluted to the mark.

The first few solutions made in this way were subjected to the following tests :

A portion of the solution was carefully evaporated to small bulk and hydrogen sulphide passed into the liquid. No precipitate formed.

Another portion of the solution was evaporated to a few cubic centimeters, ammonia added, and the test-tube stood upon white paper. No blue color.

A third portion of the solution after evaporation was placed in a bright platinum dish, a drop of nitric acid added and a weak current passed through the solution. After one hour no copper stain appeared on the dish and the platinum was still bright.

The results given by the first solution made when checked by volumetric and gravimetric methods are given below :

An exactly tenth-normal solution of sodium carbonate, made by igniting pure bicarbonate and then dissolving 5.305 grams of

the resulting sodium carbonate in a liter of water, was first used.

Check No.	Sodium carbonate solution taken. cc.	Sulphuric acid solution required to neutralize. cc.
I	25.0	25.0
2	25.0	25.1
3	15.0	15.05
4	15.0	14.9

A tenth-normal sodium hydroxide solution was next used. This solution was made by dissolving freshly cut clean bright pieces of metallic sodium in water contained in a silver dish and covered with a large inverted funnel. It was preserved in a large bottle and drawn off for use by means of a siphon passing through the stopper of the bottle. All air entering the bottle passed through a soda-lime tube, capped when not in use. This sodium hydroxide solution had been checked against a fifth-normal hydrochloric acid solution which in its turn had been standardized by precipitation with silver nitrate. It was also checked by the copper sulphate and battery method of Hart and Croasdale. These checks established a factor 0.99501, for converting to tenth-normal.

Check No.	Sodium hydroxide solution taken. cc.		Equivalent volume of N/10 solution. cc.	Sulphuric acid solution required. cc.
I	10 $\times$ 0.995	=	9.95	10.0
2	10 $\times$ 0.995	=	9.95	9.9
3	20 $\times$ 0.995	=	19.9	19.9

Finally 25 cc. of the sulphuric acid solution were acidified with a few drops of hydrochloric acid, heated to boiling, and an excess of a hot 10 per cent. solution of barium chloride slowly added with constant stirring. After standing all night the precipitate was filtered off, ignited, and weighed.

    1. Weight of barium sulphate...........................0.2923 gram.

The molecular weight of barium sulphate is 233.46 ; hence, 25 cc. of a tenth-normal solution should give $\dfrac{233.46 \times 25}{2 \times 10 \times 1000}$ = 0.29183 gram barium sulphate. The solution is therefore a little under tenth-normal, or 2923 : 2918 :: x : 1 ; x = 1.002, which gives the factor for converting to tenth-normal.

    2. Weight of barium sulphate.....................,..........0.2938 gram.
    Factor is in this case...................,.....................1.003
    Average factor for the two determinations..............1.0025

Of course results by precipitation with barium sulphate would be worthless, if the absence of copper had not been previously proved.

Since making this solution, the writer has repeatedly made normal and fifth-normal solutions by this method; it was not until recently though, that he had occasion to make a normal solution. In this case, 124.87 grams of copper sulphate were dissolved in 800 cc. of water and decomposed by a current of 2.5 amperes. The decomposition was complete in about twelve hours, though the current was allowed to run nearly eighteen. After making up to a liter, the strength of the solution was taken against the sodium carbonate solution mentioned above with the following results:

Sulphuric acid solution taken. cc.	Sodium carbonate solution required. cc.
5.0	50.1
5.0	50.2
5.0	49.8
5.0	49.95
	Average, 50.025

100 cc. of the normal solution were then diluted to 1000 cc. in a graduated flask, and after mixing tested against the N/10 sodium hydroxide solution mentioned above.

Sodium hydroxide solution taken. cc.			Equivalent volume of N/10 alkali solution. cc.	Sulphuric acid required. cc.
10.0	×	0.995 =	9.95	10.1
10.0	×	0.995 =	9.95	10.0
10.0	×	0.995 =	9.95	10.0
10.0	×	0.999 =	9.95	9.95
10.0	×	0.995 =	9.95	9.95
			Average,	10.00

All of the solutions made by this method have been checked against the sodium hydroxide solution, with the result that the strength of the sulphuric acid solution is always the desired one.

A COMPARATIVE METHOD FOR DETERMINING THE FUSING-POINTS OF ASPHALTS.

By Charles F. Mabery and Otto J. Sieplein.

SINCE all asphaltic bodies are complex mixtures of hydrocarbons with different melting-points, it is evidently quite out of the question to determine even approximately the melting-points of the asphaltic mixtures. The elements of time and temperature must be taken into account. A product that softens slowly under the influence of a summer's sun, may not fuse completely below 100° under the influence of heat suddenly applied.

The methods for determining these melting-points hitherto employed by manufacturers and consumers are extremely crude ; such for example as inserting a thermometer into the melted material, allowing the adhering mass to harden, and then holding it over a flame and noting the temperature at which it softens and falls off. Every manufacturer, therefore, and those who use his products, have felt an imperative need of a method that should enable them to ascertain with some degree of accuracy the quality of every quantity of material produced. Such a method must be simple and capable of application by any person who is able to read a thermometer. There must be few variable elements, which would affect seriously the accuracy of the observation, and those that must remain constant must be clearly defined.

Having been called upon to suggest a method that should fulfil these requirements, one of us (Mabery) proposed the one to be described which seems to promise reliable results. In a glycerine-bath in a beaker of moderate size is placed a narrow beaker closed with a cork through which is passed a thermometer. There is also inserted through the cork close to the side of the narrow beaker, a strip of metal, one-half inch wide, bent over the side of the beaker as a support, and extending to within ½ inch of the bottom of the beaker. The lower end of the metal strip is bent at right angles and the narrow corners are bent upwards. The bend in the metal is used as a support for the section of

asphalt, which is pressed on the points, formed by the corners of the metal. The dimensions of the apparatus used by us are given, but evidently the only constants need be the distance of the thermometer from the specimen, the distance of the metal from the bottom of the beaker, the width of the metal strip, and the dimensions of the specimens to be tested. With the metal strip $\frac{1}{2}$ inch wide the specimen to be tested is cut or molded of sufficient lengh to project $\frac{1}{4}$ inch on either side of the metal. The observation consists in noting the temperature at which the specimen softens and becomes sufficiently fluid to fall on either side of the metal support and just touch the bottom of the beaker. The dimensions of the different parts of the apparatus are given with the illustration. We found it convenient to place a disk of copper or iron on the bottom of the inside beaker, since it could be removed after the observation, and the asphalt that had fallen more conveniently cleaned than from the bottom of the beaker. While a Bunsen gas flame is the more convenient source of heat, an alcohol or an oil lamp can be used when gas is not at hand. Evidently the time of heating should not vary widely, although we have found as will appear that a variation of five minutes had no appreciable effect on the melting-points.

The apparatus used in the determinations described in this paper had the following dimensions which are given in inches that they may be readily understood by any manufacturer. The only dimensions that must be constant were mentioned above :
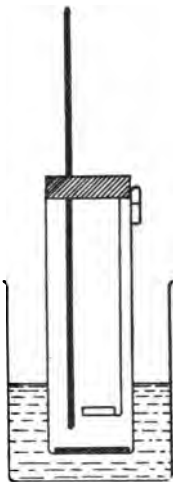
	Inches.
Width of outside beaker	$2\frac{1}{2}$
Height of "	$3\frac{1}{4}$
Width of inside beaker	$1\frac{5}{8}$
Height of "	$4\frac{1}{4}$
Width of metal support	$\frac{1}{2}$
Length of lower bend of support	$\frac{5}{8}$
Distance of specimen from false bottom of beaker	$\frac{1}{4}$
Distance of thermometer from specimen	$\frac{1}{4}$
Standard size of specimen	$1 \times \frac{1}{2} \times \frac{1}{4}$

In testing the efficiency of this method, the fusing-points of a variety of asphaltic materials were determined. Observations were made of the initial temperature, of the temperature at the time when the softened material just touched the bottom of the beaker, and of the time of heating. The effect of varying the dimensions of the specimen on the fusing-point was also observed.

Specimen 1, byerlyte.

Dimensions of specimen, $1'' \times \frac{1}{2}'' \times \frac{1}{4}''$.

(1) Time, ten minutes; temperatures, 30°–132° fusing-point.

(2) Dimensions of specimen, $1'' \times \frac{1}{2}'' \times \frac{1}{8}''$. Time, five minutes; temperatures, 20°–131° fusing-point.

To determine the influence of thickness, the following experiments were made with the same material as in (1) and (2):

(3) Dimensions, $\frac{3}{4}'' \times \frac{1}{2}'' \times \frac{1}{4}''$; time, eleven minutes; temperatures, 40°–139° fusing-point.

(4) Dimensions, $\frac{3}{4}'' \times \frac{1}{2}'' \times \frac{1}{8}''$; time, 14 minutes; temperatures, 60°–137° fusing-point.

(5) Dimensions, $\frac{3}{4}'' \times \frac{1}{2}'' \times \frac{1}{16}''$; time, ten minutes; temperatures, 30°–135° fusing-point.

Evidently variation in thickness within these limits has little effect on the fusing-point.

The effect of even higher initial temperature was shown in the following experiments on the same material as in (4), with the same dimensions.

(6) Time, eight minutes; temperatures, 50°–135° fusing-point.

(7) Time, nine minutes; temperatures, 70°–135° fusing-point.

Specimen 2, slightly less fusible; same dimensions as in (4).

(8) Time, six minutes; temperatures, 45°–138° fusing-point.

(9) Time, seven minutes; temperatures, 45°–142° fusing-point.

Specimen 3, byerlyte.

(10) Time, twelve minutes; temperatures, 30°–174° fusing-point.

(11) Time, eleven minutes; temperatures, 40°–175° fusing-point.

A series of fusing-points were taken in a bath maintained at a constant temperature, approximately 180°. In all the following determinations the specimens were one inch in length:

(12) Same material as in (1) ; time, six minutes ; temperatures, 40°-130° fusing-point.

(13) Specimen 4, soft byerlyte ; time, three minutes ; temperatures, 20°-95° fusing-point.

(14) Same starting with cold bath ; time, five minutes ; temperatures, 20°-95° fusing-point.

(15) Same as (13); time, five minutes ; temperatures, 35°-95° fusing-point.

Specimen 5, very hard, nail made no impression.

(16) Starting with cold bath ; time, ten minutes ; temperatures, 40°-142° fusing-point.

(17) Same as (16) ; time, eight minutes; temperatures, 50°-145° fusing-point.

(18) Same as (16) and (17), bath at 180°; time, four minutes ; temperatures, 45°-143° fusing-point.

Specimen 6, gilsonite ; hard, slightly indented with nail.

(19) Time, three minutes ; temperatures, 55°-100° fusing-point.

Same starting with cold bath :

(20) Time, four minutes ; temperatures, 20°-97° fusing-point.

Same, cold bath :

(21) Time, four minutes ; temperatures, 35°-98° fusing-point.

Specimen 7, byerlyte, hard, indented with nail.

(22) Bath, 230°-240° ; time, seventeen minutes ; temperatures, 50°-217° fusing-point.

(23) Time, sixteen minutes ; temperatures, 30°-214° fusing-point.

Specimen 8, gilsonite, brittle.

(24) Bath, 180°; time, seven minutes; temperatures, 25°-150° fusing-point.

(25) Time, six minutes; temperatures, 30°-147° fusing-point.

Specimen 9, Trinidad asphalt, very brittle.

(26) Bath, 180° ; time, three minutes ; temperatures, 30°-105° fusing-point.

(27) Time, four minutes ; temperatures, 40°-103° fusing-point.

Specimen 10, Egyptian asphalt, very brittle.

(28) Bath, 180° ; time, three minutes ; temperatures, 45°-91° fusing-point.

(29) Time, four minutes; temperatures, 25°–90° fusing-point.

Specimen 11, hard pitch, brittle.

(30) Bath 180°; time, three minutes; temperatures, 30°–93° fusing-point.

(31) Time, three minutes; temperatures, 50°–92° fusing-point.

The substances tested in this examination differ widely as shown above in appearance and structure. Some are very brittle, others are tough and sectile. It is interesting to note that the brittle specimens have much lower fusing-points. In preparing the specimens from the sectile products it is easy to cut the section with a knife. The easier way to prepare specimens from the brittle bodies is to melt a portion and pour the proper amount into a mold of wood or metal.

Evidently the fusing-points are entirely arbitrary, depending on the size of the constants, so that by varying these constants any desirable fusing-points may be obtained. But it is quite clear from the results we have obtained that the fusing-points obtained with any constants adopted may be depended on.

The use of a hot bath as shown above gives the same values, and it saves much time where a large number of specimens may have to be tested.

Inspection of the results given above shows that the variation in fusing-points is not more than two or three degrees at most, and for the most part there is no variation. Probably by close attention to details there need not be a variation of more than one degree. But the variations of two or three degrees is sufficiently accurate for practical application, especially as compared with determination, such as that alluded to above, in which the specimen is melted on a thermometer bulb.

With reference to the dimensions of the specimens, evidently the length of the proportion projecting on either side of the support must not vary; but any slight variation in the thickness or the width does not affect the results. It is also evident that the time between the initial and fusing temperatures need not be rigidly adhered to.

For the determinations of fusing-points above the boiling-points of liquid baths, an air-bath must be used.

STUDIES ON SOLUTIONS OF TIN SALTS.

I. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE AND HYDROCHLORIC ACID.

BY S. W. YOUNG.

THE following paper contains the first results of an investigation, which I hope soon to carry further, into the static conditions existing within solutions consisting of water, acid, and stannous salt, as well as the influence of other salts on such conditions. I hope by means of the knowledge thus acquired, to make some research into the velocity of reduction of various reagents by stannous chloride solutions, and thus, possibly, throw a little light on some of the existing anomalies in the field of chemical kinetics.

For example, there remains still unexplained the curious fact observed by Noyes[1] that in the reduction of ferric chloride by stannous chloride the order of the reaction is apparently displaced by addition of hydrochloric acid from one of the third order to one of the second.

It seems to me that up to the present, sufficient attention has not been directed toward the strict definition of the reagents in inorganic investigations. One has generally been contented with determining some one concentration in the solution; e. g., hydrogen ions, or with working at great dilutions under the assumption that all of the reagent was dissociated, and that no other influences were present.

In many cases such procedure is wholly sufficient, but, as for example in the case of stannous chloride solutions where hydrolysis and complex molecule formation may (and do) enter in as complicating factors, a more accurate definition of the reagent is absolutely necessary. It was with this idea in mind that the following measurements of the electrical conductivity of solutions of stannous chloride and hydrochloric acid in water were made.

The method was the usual one of Kohlrausch with Wheatstone's bridge and telephone. The little apparatus shown in Fig. 1 served as the conductivity flask. Since the measurements ex-

1 Ztschr. phys. Chem., 16, 546 (1895).

tended through a very considerable range of concentrations it was necessary to have three such flasks with different capacities, the capacities being varied simply by using different sized glass tubing for the U-shaped parts of the flasks. Measurements were made at 25° C. in an Ostwald thermostat, and at 0° C. in an ice thermostat. The conductivities are calculated as specific conductivities in reciprocal ohms.
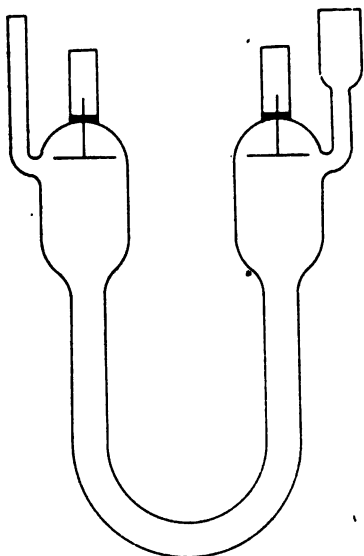
The solutions were prepared by taking a 100 cc. measuring flask, filling it to the mark with hydrochloric acid of accurately known strength. Roughly weighed amounts of pure crystallized stannous chloride were then added, brought into solution, and the liquid, made up to 105 cc. The concentration of the hydrochloric acid in the solution was thus $\frac{100}{105}$ of that of the acid used.

Fig. 1.

The concentration of the stannous salt was readily determined by titration with standard bichromate, using potassium iodide and starch paste as indicator.

Hydrochloric acids of concentrations varying from 0.25 normal to nearly 8 normal were used. With each acid from six to eight different solutions were made, varying as to concentration of stannous chloride from zero to approximately normal. No attempt was made to prepare solutions that were exactly normal, 0.5 normal, etc., because of the somewhat uncertain composition of the crystallized stannous chloride used.[1] Following (Table I), are the tabulated results of the series of measurements at 25° C. The first columns contain the concentrations of stannous chloride in gram equivalents per liter ; the second columns contain the val-

[1] A beautifully white, crystallized stannous chloride, which dissolved perfectly in pure water when the solution was not made too dilute, and whose hydrolyzed solutions cleared up immediately upon the addition of a few drops of acid, was obtained from Kahlbaum. The salt showed a distinct tendency to effloresence, and from analyses showed itself to be nearly free from impurity.

ues of the specific conductivities in $\dfrac{1}{\text{ohms}} \times 10^4$; the third columns contain the values $\dfrac{\Delta K \times 10^4}{C_{SnCl_2}}$, i. e., the change in the conductivity as a result of addition of stannous chloride, and calculated to the unit of concentration. A minus sign indicates a decrease of the conductivity, a plus sign an increase.

TABLE I.—CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE IN AQUEOUS HYDROCHLORIC ACID AT 25° C.

With ¼ normal HCl.[1]			With ⅓ normal HCl.			With ½ normal HCl.		
$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$
0.000	900.3	....	0.000	1738	....	0.000	2045	....
0.0605	914.7	+238	0.061	1738	....	0.063	2045	∞
0.1180	929.0	+243	0.122	1740	+16	0.111	2045	∞
0.1810	946.4	+255	0.247	1746	+32	0.238	2045	∞
0.2490	960.5	+242	0.366	1751	+36	0.391	2045	∞
0.3125	977.4	+247	0.465	1756	+39	0.607	2040	—8
0.5830	1041.0	+243	0.575	1759	+37	0.920	2032	—14
1.1050	1123.0	+202	1.045	1794	+46	....	....	....

With ¾ normal HCl.			With normal HCl.			With 1¼ normal HCl.		
$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$
0.000	2495	.....	0.000	3205	.....	0.000	3860	.....
0.058	2493	—34.5	0.013	3202	—231	0.066	3848	—182
0.119	2489	—50.0	0.053	3190	—283	0.192	3827	—172
0.240	2479	—64.0	0.100	3187	—180	0.310	3805	—177
0.345	2473	—64.0	0.3125	3157	—157	0.475	3782	—164
0.475	2462	—70.0	0.4950	3128	—155	0.665	3748	—169
0.585	2457	—65.0	0.700	3107	—140	0.990	3700	—162
0.990	2425	—70.0	1.000	3093	—117	....	....	.....

With 1¾ normal HCl.			With 2 normal HCl.			With 2¼ normal HCl.		
$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$C \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$
0.000	4447	.....	0.000	5478	.....	0.000	6330	.....
0.070	4429	—257	0.073	5456	—301	0.064	6305	—390
0.195	4408	—200	0.182	5434	—242	0.178	6262	—380
0.300	4389	—193	0.305	5401	—250	0.280	6244	—307
0.465	4357	—193	0.485	5352	—260	0.455	6205	—272
0.615	4332	—187	0.660	5316	—245	0.635	6152	—280
1.010	4249	—196	0.988	5226	—254	0.995	6053	—278

[1] These figures indicate the strength of the acid used in making the solutions and are to be multiplied by 111/118 in order to get actual concentration in the solution as prepared.

With 3 normal HCl.			With 4.28 normal HCl.			With 7.7 normal HCl.		
$c \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$c \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$c \dfrac{SnCl_2}{2}$	$\curlywedge 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$
0.000	6985	.....	0.000	8050	.....	0.000	8250	.....
0.065	6963	—336	0.060	8032	—300	....	....	.....
0.192	6916	—360	0.151	7997	—351	. ..	....	.....
0.300	6882	--343	0.236	7971	—336	....	....	.....
0.420	6850	—321	0.415	7907	—340	....	....	.....
0.580	6803	—314	0.560	7866	—327	....	....	.....
0.995	6686	—300	0.885	7741	—349	0.985	7854	—402

In Table II are collected the results of an exactly similar set of measurements, carried out at 0° C. In this set of observations only four concentrations of stannous chloride for each concentration of hydrochloric acid were used, and some concentrations of hydrochloric acid measured at 25° C. were omitted from this set.

TABLE II.—CONDUCTIVITY OF SOLUTIONS OF STANNOUS CHLORIDE IN AQUEOUS HYDROCHLORIC ACID AT 0° C.

With ½ normal HCl.			With ½ normal HCl.			With normal HCl.		
$c \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$c \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$c \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$
0.000	580.1	.....	0.000	1117	....	0.000	2074	....
0.272	620.0	+147	0.295	1126	+30	0.449	2032	—93
0.655	664.9	+130	0.745	1134	+23	0.770	2009	—84
1.045	701.3	+115	1.165	1141	+21	1.090	1981	—76

With 2 normal HCl.			With 3 normal HCl.			With 4 normal HCl.		
$c \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$c \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$	$c \dfrac{SnCl_2}{2}$	$K \times 10^4$.	$\Delta K \times 10^4$.
0.000	3545	.....	0.000	4535	....	0.000	5160	....
0.290	3500	—155	0.327	4482	—160	0.293	5095	—222
0.690	3432	—164	0.710	4404	—184	0.670	5010	—224
1.005	3378	—166	1.035	4341	—188	0.965	4939	—229

With 5.79 normal HCl.		
$c \dfrac{SnCl_2}{2}$.	$K \times 10^4$.	$\dfrac{\Delta K \times 10^4}{C}$
0.000	5600	....
0.290	5509	—313
0.660	5411	—290
1.025	5293	—301

In Table IIIa, is given a summary of the results given in Table I for normal solutions of stannous chloride. In the first column are the concentrations of the hydrochloric acid used in making

up the solutions; in the second column the conductivities in $\dfrac{1}{\text{ohms}} \times 10^4$ for solutions containing no stannous chloride; in the third column the corresponding values for solutions whose concentrations in stannous chloride were approximately normal; in the fourth column the differences of the first two columns divided by the actual concentration of the stannous chloride (always very near to normal); *i. e.*, the *equivalent influence of stannous chloride upon the conductivity of hydrochloric acid solutions*; in the fifth columns the same values calculated in percentages of the conductivity of the pure hydrochloric acid solution.

Table III*b* contains the same results for the measurements at 0° C.

TABLE III*a*.—SUMMARY OF VALUES OF CHANGES IN CONDUCTIVITY OF HYDROCHLORIC ACID BY NORMAL STANNOUS CHLORIDE AT 25° C.

C_{HCl}.	$K \times 10^4$. $SnCl_2 = 0$.	$K \times 10^4$. $SnCl_2 = N$.	$\dfrac{\Delta K \times 10^4}{C_N}$	Per cent.
0.25 N	900.3	1123	+202	+22.44
0.50	1738	1794	+ 46	+ 2.17
0.60	2045	2032	— 13	— 0.60
0.75	2495	2425	— 70	— 2.81
1.00	3205	3093	—117	— 3.64
1.25	3860	3700	—162	— 4.20
1.50	4447	4249	—196	— 4.41
2.00	5478	5226	—254	— 4.50
2.50	6330	6053	—278	— 4.40
3.00	6985	6686	—300	— 4.35
4.28	8050	7741	—349	— 4.02
7.70	8250	7854	—402	— 4.81

TABLE III*b*. CORRESPONDING VALUES AT 0° C.

C_{HCl}.	$K \times 10^4$. $SnCl_2 = 0$.	$K \times 10^4$. $SnCl_2 = N$.	$\dfrac{\Delta K \times 10^4}{C_N}$	Per cent.
0.25 N	580.1	701.3	—115	+19.82
0.50	1117	1141	+ 21	+ 1.85
1.00	2074	1981	— 76	— 3.67
2.00	3545	3378	—166	— 4.68
3.00	4535	4341	—188	— 4.14
4.00	5160	4939	—229	— 4.44
5.79	5600	5293	—301	— 5.38

The following curves will make the relationships between the values given in the tables, somewhat more readily comprehensible. In the set of curves, Fig. 2, are plotted as abcissas, the concen-

trations of hydrochloric acid, and as ordinates the changes in the conductivity, brought about by the addition of stannous chloride. The curve with continuous line is for normality in stannous chloride, at 25° C. ; the curve with dotted line is for normality in stannous chloride at 0° C.   In the set of curves, Fig. 3, are the same values calculated to percentages.

DISCUSSION OF THE RESULTS.

The method of determining variations in the electrolytic conductivity of mixed electrolytes as a test for the formation of molecular complexes in such solutions, is by no means new. Thus, Peters[1] measured the conductivities of solutions of ferrous and ferric salts, and the influence of sodium fluoride upon the same.   From the results of his work, he concludes that complex molecules are formed in the case mentioned, and the conclusion is supported by measurements of freezing-points, transference numbers, and electromotive forces.

Also the idea, that solutions of stannous salts containing excess of acid were prone to form complex molecules in solution, is not new.   From the great increase in the solubility of stannous chloride, in solutions of increasing concentration of hydrochloric acid, Engel[2] concluded that in such solutions, the formation of complex molecules occurred.   In previous papers by me,[3] a similar condition was shown to exist for stannous iodide and hydriodic acid, and it was further shown that at moderately low temperatures, a compound, probably SnI_2HI, crystallizes out from solutions not too dilute in hydriodic acid.

That a reduction of the total conductivity of the solution to a point far beyond what is to be expected from any theory of mixed electrolytes, occurs upon the addition of stannous chloride to moderately concentrated hydrochloric acid solutions, is very definitely proved by the above measurements.   By reference to Table IIIa, it will be seen that the addition of stannous chloride, to normality, to a 0.25 normal solution of hydrochloric acid, conditions an increase of conductivity of 202 units.[4]   Neglecting the

[1] *Zeit. phys. Chem.*, **26**, 193 (1898).

[2] *Ann. chim. phys.*, **17**, 338 (1889).

[3] This Journal, **19**, 845 and 851 (1897).

[4] It is quite possible that this number is too low from some experimental error (*c.f.* Table I). It may be mentioned here, in passing, that what little evidence is at hand, seems to indicate that the hydrolysis constant of stannous chloride, is a fairly large one,

influence of this concentration, of hydrolysis, molecular complex formation, and of variations from the fact that the solutions are not isohydric, we can get a very rough idea of the magnitude of the conductivity of stannous chloride in normal solution, the value being 202, a number of a magnitude comparable with the corresponding value for cadmium bromide (about 200), or cadmium chloride (about 230). When 0.5 normal hydrochloric acid is used, the increase is only 46 units. With 0.6 normal acid there occurs

a small reduction $\left(-13\dfrac{1}{\Omega} \times 10^4 \text{ or } 0.6 \text{ per cent.}\right)$. With stron-

ger acids a reduction in the conductivity always occurs which becomes larger as the strength of the acid increases. The conduct at $0°$ C. (Table IIIb) is wholly analogous to that at $25°$ C. A curious thing is to be noticed in Fig. 3. The percentage influence of normal stannous chloride on hydrochloric acid solutions of increasing concentration shows a maximum at about double normal hydrochloric acid. From this point on, the percentage influence decreases to a minimum at about 4 normal hydrochloric acid at $25°$ C., and at about 3 normal hydrochloric acid at $0°$ C. From these minimum points on, the percentage influence again increases with increasing concentration of hydrochloric acid. The counterpart of this peculiarity is to be distinctly seen in Fig. 2. In the curve for $25°$ C., it appears as a mere flattening of the curve, while in the curve for $0°$ C., an actual change in the direction of curvature is to be seen. As to the physical significance of these peculiarities, perhaps the

and that a very considerable degree of hydrolysis occurs even in moderately acid solutions of the salt. It is further quite probable that the hydrolysis is a reaction requiring a very considerable amount of time for its completion. Both of these statements are rendered likely from the results of the following experiment: A 0.2 normal solution of hydrochloric acid was taken, and to it, some stannous chloride was added. The solution was then placed in the conductivity flask (Fig. 1), and placed in the thermostat at $25°$ C. The conductivity measured immediately, was 843.7. After twenty-five minutes it was 850, after sixty-five minutes 852; and after 1100 minutes, 870.4. This increasing conductivity can easily be explained, as due to progressing hydrolysis. The solution remained clear throughout the whole time. That the phenomenon was not due to oxidation, is indicated by the fact that a similar experiment with stronger acid (0.5 normal) gave constant readings for twenty-four hours. It was also observed that rather concentrated solutions of stannous chloride have the power of dissolving very considerable quantities of hydrolyzed stannous chloride (oxychloride). Thus it appears probable that stannous chloride may become hydrolyzed to a very considerable extent without separation in an insoluble form of oxychloride. This probability is rendered greater by evidence derived from a study of the oxidation of stannous chloride to be published in a subsequent paper. If true, the fact would have an important bearing on the work of Noyes, "On the Reduction of Ferric Chloride with Stannous Chloride" (q.v.). The whole matter of hydrolysis will be made the subject of a special investigation.
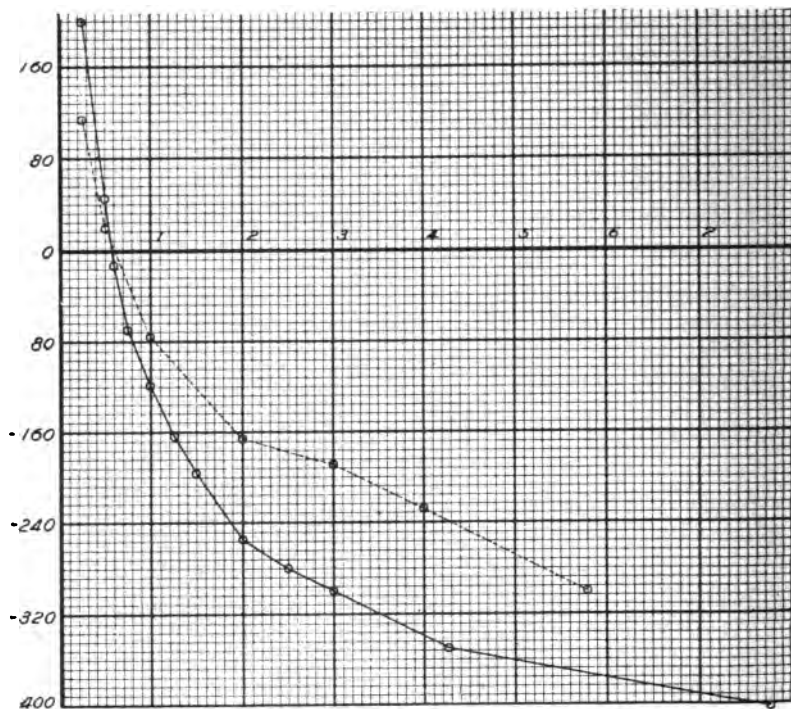
Fig. 2.

simplest and most satisfactory explanation would be to assume that in stannous chloride and hydrochloric acid solutions, there are two distinct kinds of molecular complexes formed. For example, at low concentrations, we may assume that the equilibrium, $SnCl_2 + HCl \rightleftarrows HSnCl_3$, plays the chief rôle, while at high concentrations, the equilibrium $H.SnCl_3 + HCl \rightleftarrows H_2SnCl_4$ (or some similar one) becomes more and more noticeable. In other words, we may have two equilibria, one very sensitive to dilution, the other very considerably less sensitive. Plotting these conditions graphically for the two equilibria independently of one another, in such a way that the ordinates represent the concentration of the dissociated part (left-hand members of the above equations) and abscissas either the total concentrations or undissociated concentrations, we should get curves similar to those in Fig. 4, a being for the more sensi-
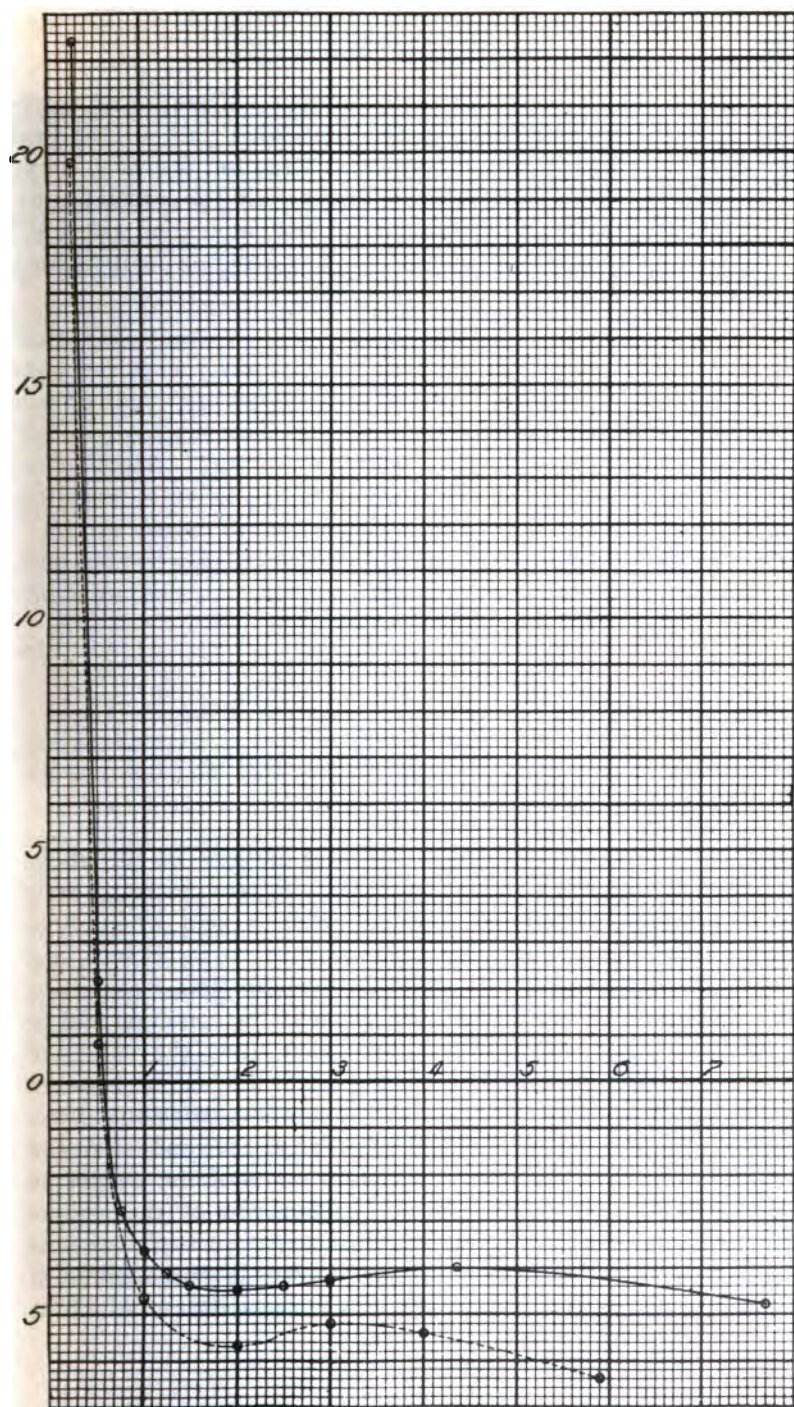
Fig. 3.

tive, and b for the less sensitive equilibrium. Then let cd represent the zero concentration for the dissociated part of the first equilibrium and ef that of the second. Then for the first curve there will be a point K' where the influence of the second equilibrium will become measurably large and a similar point K" where the measurable influence of the first reaction will become
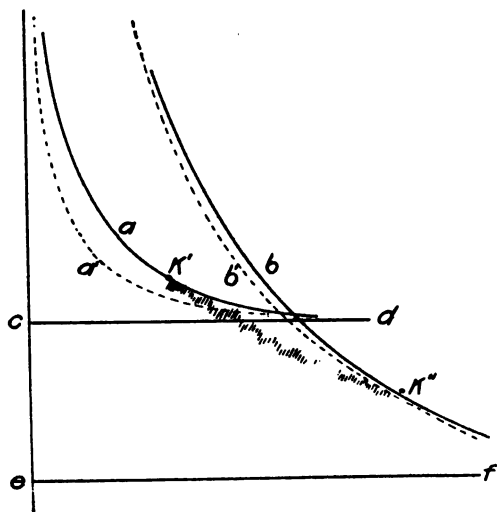
Fig. 4.

constant because one component (in the conditions of the above experiments the free stannous chloride) will have ceased to exist in the solution. Between K' and K" will be a field where both condensation products (in this case assumed to be $HSnCl_4$ and H_2SnCl_4) will be measurably removed from complete dissociation and from complete association. In this field the condition will be a resultant of the two equilibria, dependent upon the values of the two equilibrium constants. The path of the curve between K' and K" could be determined if these two constants were known. If we consider that the reduction of the conductivity of such solutions is ever qualitatively a measure of the degree of association we get a very simple explanation of the above-mentioned peculiarities. Further, also, we get an explanation of the fact that the abnormal course of the curve is more marked at 0° C. than at 25° C. if we assume that the equilibrium which is

more sensitive to dilution is also more sensitive to temperature changes (*i. e.*, has a greater heat of reaction). In this case the association consequent upon reduction of temperature will be greater in the case of the first equilibrium than in the second and the curves (Fig. 4) will take on more of the form shown in the dotted lines and the buckle in the curve will be sharper.

It may be mentioned that the above considerations are in no way in disaccord with the general principles of equilibrium. No assumption is made that the two equilibria are independent of one another, but merely that at great dilutions, the influence of the one, and at small dilutions the influence of the other, becomes insignificant. It is by the same assumption that we neglect the influence of hydrolysis in moderately acid solutions of most salts.

In the above, the *assumption* is made, for sake of illustration that the two equilibria in the solutions are represented by the two equations :

$$HCl + SnCl_2 \rightleftarrows HSnCl_3 \qquad (1)$$

and

$$HCl + HSnCl_3 \rightleftarrows H_2SnCl_4. \qquad (2)$$
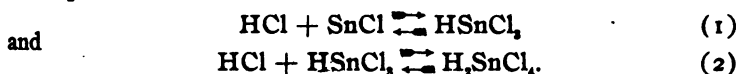
It may be stated that, so far as the work has gone at present, there is no particular evidence that this assumption is well founded. All the evidence that we really have as to the probable composition of these molecular complexes, comes from our knowledge of the molecular complexes that are known to exist in the solid state, such as Engel's (1. c.) $SnCl_2.HCl.3H_2O$, iodostannous acid, $HSnI_3$, and the various double salts of tin, and we have really no ground for assuming that the complexes that exist in solution, stand in any fixed or simple relation to those that exist in the solid state. Only further investigation will be able to clear up these points.

THE INFLUENCE OF POTASSIUM CHLORIDE.

The following measurements were made with the view of gaining some idea as to the relative tendencies of potassium chloride and hydrochloric acid to form molecular complexes with stannous chloride. The difficulties of calculation of this influence from conductivity data are, as will be seen, very considerable.

In Table IV*a* are given measurements of the conductivities of solutions of stannous chloride in solvents which were always 0.5

normal in hydrochloric acid and of varying concentrations as to potassium chloride. In Table IV*b* are similar measurements for solvents of normal concentration in hydrochloric acid and variable potassium chloride. Table V contains a summary of values from these two tables for normality in stannous chloride.

TABLE IV*a*. INFLUENCE OF KCl.

RESULTS WITH ½ NORMAL HCl.

⅓ normal KCl.			⅔ normal KCl.		
$C\frac{SnCl_2}{2}$.	$K \times 10^4$.	$\frac{\Delta K \times 10^4}{C}$.	$C\frac{SnCl_2}{2}$.	$K \times 10^4$.	$\frac{\Delta K \times 10^4}{C}$.
0.000	1871	.....	0.000	2152	....
0.0255	1868	—117	0.066	2146	—91
0.058	1866	—86	0.200	2144	—40
0.147	1874	+20	0.328	2142	—35
0.312	1878	+21	0.430	2141	—26
0.488	1879	+16	0.565	2138	—25
1.045	1898	+26	1.015	2132	—20

Normal KCl.			2 normal HCl.		
$C\frac{SnCl_2}{2}$.	$K \times 10^4$.	$\frac{\Delta K \times 10^4}{C}$.	$C\frac{SnCl_2}{2}$.	$K \quad 10^4$.	$\frac{\Delta K \times 10^4}{C}$.
0.000	2498	.....	0.000	3285	.....
0.037	2493	—135	0.032	3275	—312
0.0535	2490	—149	0.057	3266	—333
0.1140	2478	—175	0.165	3251	—210
0.1265	2477	—167	0.296	3228	—190
0.2520	2473	—99	0.465	3200	—180
0.5050	2455	—79	0.770	3147	—178

TABLE IV*b*. INFLUENCE OF KCl.

RESULTS WITH NORMAL HCl.

¼ normal KCl.			½ normal KCl.		
$C\frac{SnCl_2}{2}$.	$K \times 10^4$.	$\frac{\Delta.K \times 10^4}{C}$.	$C\frac{SnCl_2}{2}$.	$K \times 10^4$.	$\frac{\Delta K \times 10^4}{2}$.
0.000	3324	.....	0.000	3485	.....
0.062	3311	—210	0.061	3473	—197
0.174	3295	—166	0.158	3459	—165
0.293	3283	—140	0.276	3442	—155
0.438	3265	—135	0.405	3420	—160
0.565	3247	—136	0.560	3398	—154
0.978	3199	—126	0.980	3339	—149

Normal KCl.			2 normal KCl.		
$C\frac{SnCl_2}{2}$.	$K \times 10^4$	$\frac{\Delta K\, 10^4}{C}$.	$C\frac{SnCl_2}{2}$.	$K \times 10^4$.	$\frac{\Delta K \times 10^4}{C}$.
0.000	3758	.....	0.000	4437	.....
0.062	3741	−274	0.061	4419	−295
0.116	3731	−233	0.148	4398	−264
0.235	3714	−187	0.270	4368	−255
0.398	3684	−186	0.387	4336	−260
0.590	3649	−184	0.585	4292	−247
1.000	3571	−187	1.005	4193	−244

TABLE V. SUMMARY OF RESULTS WITH KCl FOR NORMAL SnCl₂.

½ normal HCl.

C_{KCl}.	$K \times 10^4$. $SnCl_2 = 0$.	$K \times 10^4$. $SnCl_2 = N$.	$\frac{\Delta K \times 10^4}{C_N}$.	Per cent.
0.25 N	1871	1898	+ 26	+1.39
0.50	2152	2132	− 20	−0.93
1.00	2498	2455	− 79	−3.16
2.00	3285	3147	−178	−5.42

Normal HCl.

C_{KCl}.	$K \times 10^4$. $SnCl_2 = 0$.	$K \times 10^4$. $SnCl_2 = N$.	$\frac{\Delta K \times 10^4}{C_N}$.	Per cent.
0.25 N	3324	3199	−126	−3.82
0.50	3485	3339	−149	−4.33
1.00	3758	3571	−187	−4.98
2.00	4437	4193	−244	−5.50

An inspection of these results discloses a distinct tendency for the values of $\frac{\Delta K \times 10^4}{C}$ to decrease with C (the concentration of stannous chloride). This is also noticeable in the results for hydrochloric acid alone, although in a much less degree. So small is the variation in those results, that it might be considered within the experimental error. In the results with potassium chloride, the variations are more marked, and although the values of $\frac{\Delta K \times 10^4}{C}$ at small concentrations of stannous chloride are sub-ject to great error, nevertheless, the perpetual recurrence of these variations in all sets of measurements, and in the same direction, would seem to indicate that they are not wholly experimental. Particularly noticeable is this variation in the case of 0.5 normal hydrochloric acid, and 0.25 normal potassium chloride, where at small concentrations of stannous chloride, a reduction of the con-

ductivity, at larger concentrations an increase in conductivity, occurs. Since the variable factors in such solutions are so numerous, one might formulate a half dozen explanations of·these peculiarities, which would be a process of very little value. However, it is to be expected from the general ideas of equilibrium that the reduction of conductivity *per unit of concentration* of stannous chloride would. be a quantity which would decrease with increasing concentration.

When we come to compare the values of $\dfrac{\varDelta K \times 10^4}{C\,(=N)}$ for these solutions (Table 5) in $\dfrac{1}{\Omega}$'s and in percentages, with those for hydrochloric acid alone (Table IIIa), we find difficulty in deciding upon a basis for this comparison.

Probably as satisfactory a method as any will be to compare the percentage effects of addition of stannous chloride to solvent containing the same concentration of chlorine. Thus the percentage change on adding stannous chloride to normality to a solution of 0.75 normal hydrochloric acid is — 2.81 per cent., and to a 0.25 normal KCl. 0.5 normal HCl the change is +1.39 ; for a normal hydrochloric acid, — 3.64 per cent.; for a 0.5 normal KCl. 0.5 normal HCl, — 0.93 per cent.; for a 1.5 normal hydrochloric acid, — 4.41 per cent.; for a normal KCl. 0.5 HCl, — 3.16 per cent.; for 2.5 HCl, — 4.40 per cent.; 2 normal KCl. 0.5 normal HCl, — 5.42 per cent. With the results for normal hydrochloric acid and potassium chloride we find : for 1.25 normal HCl, — 4.20 per cent.; for normal HCl.0.25 KCl, — 3.82 per cent.; for 1.5 normal HCl, — 4.41 per cent.; for normal HCl. 0.5 KCl, — 4.33 per cent.; for 2 normal HCl, — 4.50 per cent.; for normal HCl. normal KCl, — 4.98 per cent ; for 3 normal HCl, — 4.35 per cent ; for normal HCl.2 normal KCl, — 5.5 per cent.

By this method of comparison, it would seem that, at small concentrations, the influence of potassium chloride was less than that of hydrochloric acid, but that it increases more rapidly with the concentration and exceeds that of hydrochloric acid at greater concentrations. In this connection, it is to be said, however, that this method of calculation is sure to give results favoring the greater influence of hydrochloric acid, particularly at small concentrations of potassium chloride, since under these

circumstances the larger part of the conductivity is due to hydrochloric acid, and although the influence of the small quantity of potassium chloride might be relatively large, it would still show as but a small percentage of the whole conductivity. I have also calculated the influence of potassium chloride by one or two other methods which may be considered as rough approximations, and have invariably found that at least at high concentrations potassium chloride seems to act more strongly in producing molecular complexes than does hydrochloric acid. The whole point might be easily settled, if we could prepare isohydric solutions of stannous chloride, hydrochloric acid, and potassium chloride. The trouble is however that, apart from the interference of hydrolysis in stannous chloride solutions, we have at present no means of telling what solution of stannous chloride would contain chlorine ions at the same concentration as a given solution of hydrochloric acid. This might be determined by measurements of electromotive force, but I have not as yet been able to devise a method for this purpose that works satisfactorily with stannous chloride. Silver and silver chloride electrodes will not work, because, although silver chloride is not noticeably reduced by stannous chloride, nevertheless the reduction potential between them is easily measurable and prevents the use of such an electrode for the determination of the concentration of chlorine ions.

The above data on the influence of potassium may now be applied without very serious objection to the determination of the relative influence of other salts of about the same equivalent conductivity and degree of dissociation, as for example sodium chloride, bromide, or iodide, and potassium bromide or iodide. A few measurements were made to determine the influence of potassium iodide. The results are as follows:

Normal potassium iodide + 0.5 normal hydrochloric acid gave without stannous chloride a conductivity of 2633.

On addition of stannous chloride to 0.09 normal the conductivity fell to 2594, which gives $\dfrac{\Delta K \times 10^4}{C} = -433$. Potassium chloride under the same circumstances gave $\dfrac{\Delta K \times 10^4}{C} = -175$.

A further addition of stannous chloride to the above solution caused separation of red stannous iodide in solid form.

A second set of measurements carried out with 0.5 normal KI + 4 normal HCl gave :

$c\frac{SnCl_2}{2}$.	$K \times 10^4$.	$\frac{\Delta K \times 10^4}{c}$.
0.000	7918	.....
0.119	7866	—433
0.304	7785	—435
0.950	7515	—424

These values are considerably greater than for hydrochloric acid alone of 4.28 normal concentration ; *viz.*, — 330 to — 350, and they are noticeably greater than the values for even hydrochloric acid of 7.7 normal; *viz.*, — 402. It is hoped soon to investigate this field more thoroughly.

From the results of the foregoing measurements we may consider the following conclusions as probable :

(1) Stannous chloride and hydrochloric acid form molecular complexes in solution, the formation of such complexes increasing with the concentration.

(2) In so far as reduction of electrical conductivity may be taken as a measure of such association, evidence is shown of the existence of two distinct forms of association, one being considerably more sensitive to dilution than the other ; *i. e.*, having a larger dissociation constant.

(3) Potassium chloride shows a greater power of association at large concentrations than does hydrochloric acid, and it is quite probable that the same will be found to be true at lower concentrations also.

(4) From what evidence is at hand, potassium iodide shows a still greater influence in the direction of forming complex substances in solutions of stannous chloride. This is in keeping with the well-known behavior of iodides in forming double salts.

It has been my pleasure to have carried out the above investigation in the laboratory of the Physical-Chemical Institute, at Leipzig. I wish to take this opportunity to thank the director of the institute, Prof. Ostwald, and the assistants in the institute, especially Drs. Bredig and Luther, for the kindly consideration and timely suggestions which they gave me during my all too brief stay at Leipzig.

A MODIFICATION OF THE USUAL METHOD OF DETER-MINING TRANSFERENCE NUMBERS, AND AN INVESTIGATION OF THE INFLUENCE OF THE CONCENTRATION ON THEIR VALUES IN THE CASE OF SOME TRI-IONIC SALTS.

BY ARTHUR A. NOYES.

I. PURPOSE OF THE INVESTIGATION.

AS has been frequently pointed out, the dissociation of tri-ionic salts, such as potassium sulphate and barium nitrate, like that of most dibasic acids, might well be expected to take place in the two stages expressed by the following equations :

$$K_2SO_4 \rightleftarrows K^{\cdot} + KSO_4', \text{ and } KSO_4' \rightleftarrows K^{\cdot} + SO_4'' ;$$

$$Ba(NO_3)_2 \rightleftarrows BaNO_3^{\cdot} + NO_3' \text{ and } BaNO_3^{\cdot} \rightleftarrows Ba^{\cdot\cdot} + NO_3'.$$
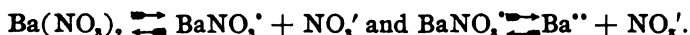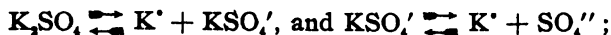
Up to the present time, however, no conclusive experimental evidence of the existence of such intermediate complex ions as KSO_4' and $BaNO_3$ has been presented. The freezing-point lowering and electrical conductivity of such salts prove, to be sure, that, even in moderately concentrated solutions, the intermediate ions, if they exist at all, are present only in relatively small amounts. Nevertheless, the question is still unanswered, whether the portion of the salt that is not completely dissociated consists wholly of undissociated molecules (K_2SO_4 and $Ba(NO_3)_2$) or mainly of the partially dissociated ones (KSO_4' and $BaNO_3^{\cdot}$). The answer to this question cannot be reached by the method used in the case of dibasic acids, since it is only for hydrogen and hydroxyl ions that we possess specific quantitative methods of determination. The property adapted to throw the most light on the matter would seem to be the change of the transference numbers of such salts with the concentration ; for, if KSO_4' or $BaNO_3^{\cdot}$ ions exist in moderately concentrated solution, and if these ions are dissociated in diluter solutions, as they must be, into $K^{\cdot}$ and SO_4'' or $Ba^{\cdot\cdot}$ and NO_3' ions, it is evident that the proportion of potassium or barium transferred in the differently concentrated solutions will be markedly different. This investiga-

tion was, therefore, undertaken in order to determine the effect
of dilution on the transference numbers of some tri-ionic salts.
Since the results, to be of much value in connection with the
theoretical question just referred to, must have a high degree of
accuracy, my first efforts were, however, devoted to perfecting
the usual method of determining transference numbers, and these
have led to a modification of it, which it is one of the main pur-
poses of this article to describe.

2. RESULTS OF PREVIOUS INVESTIGATORS.

Before describing my own experiments, the results of previous
investigators bearing directly on the subject may be mentioned.

In the first place, it may be recalled that various investigators
have proved that the transference numbers of *di*-ionic salts do not
vary with the concentration, provided the latter does not exceed
a moderate value ; for example, 0.5 mol per liter. Thus, this has
been shown by Hittorf in the case of potassium chloride, bro-
mide, iodide, chlorate, nitrate, cyanide and acetate, ammonium
chloride, sodium chloride, nitrate and acetate, and silver nitrate.
This constancy of the transference numbers has been confirmed
by other investigators[1] in the case of many of these salts, and has
been found by Loeb and Nernst[2] to apply also to silver acetate
and silver ethyl sulphate. The only exceptions thus far discov-
ered are in the cases of lithium iodide and chloride which have
been found by Kuschel[3] and Bein[4] to behave like the halides of
the alkaline earth metals (see below). Aside from these excep-
tions, which are probably to be explained by assuming the forma-
tion of intermediate complex ions, the statement made above in
regard to the non-variation of transference values with the dilu-
tion holds true.

Hitherto only very few tri-ionic salts have been satisfactorily
investigated in this direction. Aside from the earlier experi-
ments of Hittorf, Weiske, Kuschel, and others, which are not
sufficiently accurate to throw any light on the present question,[5]

[1] For the original literature on transference determinations see Bein : *Ztschr. phys.
Chem.*, 27, 1. For a summary of all existing values for concentrations up to 0.1 normal, see
Kohlrausch : Wied. *Ann.*, 66, 816.

[2] *Ztschr. phys. Chem.*, 2, 948.

[3] Wied. *Ann.* 13, 289.

[4] *Ztschr. phys. Chem.*, 27, 50.

[5] Compare Bein : *Ztschr. phys. Chem.*, 28, 439-452, in regard to the errors of the early
determinations ; also Kohlrausch : Wied. *Ann.*, 66, 818, in regard to the disagreement of
he results.

and aside from the more recent experiments on the halogen compounds of cadmium and zinc, which exhibit unusually complicated relations, the only determinations available for our purpose are those of Bein[1] on barium, strontium and calcium chlorides and of Hopfgartner[2] on barium chloride. It is desirable that even these determinations should be confirmed, since the results obtained are somewhat remarkable in their character. It was found, namely, that the transference number of the cathion increases with increasing dilution, which is just the opposite of the effect which would arise from the presence of BaCl' or CaCl' ions in the more concentrated solution. Barium chloride was, therefore, included among the salts which I have investigated. The significance of the behavior which it exhibits will be further considered below.

3. DESCRIPTION OF THE METHOD.

As is well known, the principal difficulty met with in determining the transference numbers of salts for which electrodes of the same metal cannot be used, arises from the fact that free alkali and acid are generated at the cathode and anode respectively, and that the hydroxyl and hydrogen ions thus produced, on account of their high rates of migration, rapidly pass into the middle portions of the solution, thus changing its composition and its transference relations.[3] This change in composition can be greatly retarded on the anode side by the use of a cadmium electrode, since the cadmium ions that pass into solution have a rate of migration very much smaller than that of hydrogen ions. This kind of anode has, in fact, been generally employed.[4] There has been, however, no equally satisfactory method described for preventing the dispersion of the hydroxyl ions produced at the cathode, and Hittorf, Bein, and others in their investigations have simply taken care to stop the electrolysis before the alkali reached the middle portions.

[1] *Ztschr. phys. Chem.*, 27, 50, 51.
[2] *Ibid.*, 25, 137.
[3] See Bein (*Ztschr. phys. Chem.*, 27, 3–18) for a full discussion of this matter.
[4] Compare Bein (*Ztschr. phys. Chem.*, 27, 21) in regard to the source of error arising from the deposition of smal quantities of basic salt on the anode.
[5] Both Lenz and Hopfgartner, with this purpose in view, covered the cathode, which consisted of mercury, with concentrated zinc chloride solution, but this prevented an accurate analysis of the solution around the cathode.

This procedure is, however, open to the objection that the absolute amount of substance transferred is necessarily small, and since this small amount is obtained as a difference of two much larger experimentally determined quantities, the percentage errors in the final results are necessarily large. Thus in Bein's experiments on metallic chlorides, which are probably the most accurate with polarizable electrodes thus far published, the amount of chlorine transferred was in almost all cases between 9 and 40 milligrams, and this value was obtained by taking the difference between two quantities usually four to ten times as great. It is true, to be sure, owing to the great accuracy of the volumetric determination of chlorine, that the corresponding transference values exhibit an average deviation from the mean of only 0.6–0.7 per cent.[1] This degree of accuracy could probably not be reached in the case of most other ions, and even it leaves very much to be desired.

It occurred to me now that the difficulty just considered, arising from the dispersion of the hydrogen and hydroxyl ions into the solution, might be entirely obviated by the simple device of gradually adding during the electrolysis to the solutions around the cathode and anode, sufficient amounts of the acid and base, respectively, of which the salt is composed, to keep those solutions neutral (or, preferably in practice, slightly acid and alkaline respectively). If, furthermore, the acid and base added are dissolved in suitable quantities of water, it is evident that not only the formation of new substances around the electrode may be prevented, but also that the changes of concentration of the original salt due to transference may be compensated, so that the whole solution will remain unchanged in composition, and the electrolysis can be continued indefinitely. Thus if the transference number (which is approximately 0.5) of a 0.2 normal potassium sulphate solution were to be determined, one would add gradually at the cathode 0.4 normal sulphuric acid in such (measured) amounts, determined with the help of an indicator or calculated from the electricity passing through, as will keep the solution slightly acid ; and would add at the anode an equal amount of 0.4 normal potassium hydroxide. If, however, the transference number of the positive ion were 2/3 and the salt 0.2 normal as

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[1] This estimate is based on a consideration of Bein's results with the chlorides of the alkali- and alkaline-earth metals at ordinary temperatures (p. 49-51 of his article).

before, the acid solution used would have to be o.3 and the base solution o.6 normal, and the volume of the former added would have to be twice that of the latter, in order to keep the concentration constant. In practice, however, it is desirable that the added solutions should be somewhat stronger (or weaker) than the theory requires, in order to prevent the solution around the electrodes from rising (or sinking) into the middle portions.

Three salts, potassium sulphate, barium chloride, and barium nitrate, were investigated in the order in which they are here named, each one at two concentrations, o.1 and o.02 molar.[1] The samples used were prepared by recrystallizing the commercial chemically pure salts two or three times from water. In the case of the potassium sulphate, the analyses of the solutions, both before and after the electrolysis, were made by evaporating them, after exactly neutralizing, if necessary, with sulphuric acid to dryness on a water-bath in platinum dishes, and igniting the residue, at first very gently and then intensely. Great difficulty was experienced by reason of decrepitation on first heating; but this source of error was entirely removed by tying ash-free filter-paper closely over the top of the dish, heating carefully only the bottom of the dish so as to avoid igniting the paper, and afterwards incinerating the paper. In the case of the two barium salts, the analyses were made by adding a slight excess of sulphuric acid to the solution, evaporating to dryness as before, and igniting the residue to a constant weight at a moderate red heat. During the evaporation the dishes were covered with filter-paper (which was afterwards incinerated), in order to avoid a loss of the precipitate by spattering, occasioned by the escape of small bubbles of air from the solution. This subtle source of error caused, before it was discovered, the loss of several transference determinations. The barium hydroxide solution added at the anode was, in the case of the barium nitrate experiments, analyzed in just the same manner.

The method employed in carrying out the transference experi-

[1] I use this term (previously suggested by Ostwald) to designate the concentration of solutions containing 1 mol (one molecular weight in grams) in 1 liter of solution. The general introduction of some such term seems highly desirable, first in order to avoid a very frequently occurring circumlocution; and second, in order to avoid the serious confusion which is beginning to arise through the double use of some writers of the term *normal*; namely, its use in this sense, as well as in its appropriate sense of one equivalent per liter.

ments with barium nitrate, was somewhat different in its details from that used in the case of the other two salts. I will first fully describe the former method, for it has, I believe, some advantages over the latter ; and will then briefly mention the respects in which the two methods differ.

At the beginning of each experiment the apparatus, shown in the accompanying sketch, consisting essentially of two large glass

⅜ NAT'L SIZE
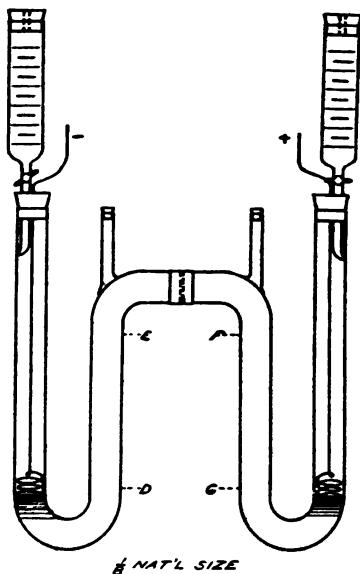
U-tubes, 3.5 cm. in diameter, joined by a piece of soft rubber tubing, was charged with such an amount of barium nitrate solution that the inside arm of the U-tubes and their outside arms up to a point about 2 cm. above the top of the bend were filled with it. Rubber stoppers were inserted in the small upright arms on the middle of the tube, so as to keep the solution in place. To the portions in the bends were added a few drops (a known weight) of phenolphthalein solution, in order to assist in regulating the addition of alkali and acid. The indicator is rapidly decolorized in the immediate neighborhood of the anode, but is nevertheless useful, since it retains its color in the bend beneath. Cork stoppers with one large and one small hole were inserted in the top of each side-arm. Through the small holes passed heavy platinum wires bent at

the bottom into the form of a spiral. These were made to dip only a few millimeters into the solution, and were gradually raised during the electrolysis so as to be always near the top of the liquid. The distance between the electrodes was 80–100 cm. Through the larger holes in the stoppers were inserted the stems of cylindrical drop-funnels, like those shown in the drawing. These were graduated with divisions corresponding to each 5 cc. The stems were bent slightly at their ends and drawn to a point, so as to cause them to remain full of liquid and to deliver against the sides of the U-tubes. These two drop-funnels were filled at the start with approximately 0.5 normal nitric acid[1] and barium hydroxide for the experiments with the more concentrated solution, and with 0.1 normal acid and base for those with the more dilute. These funnels, which were closed above with one-hole rubber stoppers, were weighed to the nearest centigram before and after the electrolysis, the stems being capped with small test-tubes during the weighing. The base solution was protected from the air during the electrolysis by a soda-lime tube inserted in the rubber stopper.

At least twenty minutes before the electrolysis was started the U-tubes were immersed in a large thermostat at 25°, to such a depth that the middle horizontal part of the apparatus was entirely covered. After the temperature differences had become equalized, 2.5 cc. of the nitric acid solution were added at the cathode and 10–15 cc. of the barium hydroxide solution at the anode. This excess of the latter was added at the start, in order to make the anode solution distinctly heavier than the middle portion above, and to introduce into the bend enough free base to neutralize any acid which might escape neutralization in the immediate neighborhood of the electrode. The electrodes were then connected through a switch, one 16-candle power 110 volt lamp, a Weston milliammeter, and a silver voltameter, all in series, with the terminals of the city circuit of 110 volts potential, and the current was turned on. The silver voltameter consisted of a platinum dish (which served as the cathode) which contained a 15 per cent. silver nitrate solution, just beneath the surface of which

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[1] The acid solution used in the first experiments was prepared by diluting the concentrated acid with pure distilled hydrogen [peroxide solution, in order to entirely prevent reduction of the nitrate to nitrite and ammonia; but this precaution was later dispensed with, as it was found to make no difference in the results.

was placed a horizontal silver plate (to serve as anode) which was wrapped with filter-paper and supported by a silver rod riveted through it. The milliammeter served merely to indicate the strength of the current, and was not used for a quantitative determination of it.

As the electrolysis proceeded, at intervals of ten to twelve minutes, each time as soon as the pink color appeared at the cathode, 2.5 cc. of the nitric acid solution and an equal volume of the barium hydroxide solution were added. The electrolysis was continued for about three hours. At the end of this time the electrodes and drop-funnels were removed, perforated rubber stoppers were inserted in the side arms, their holes were closed by pushing in pieces of glass rod, and the stoppers in the small middle arms were taken out. Through these arms three middle portions (lying between the points E and F, D and E, and F and G in the figure) were slowly removed by means of a pipette connected with a suction-pump, the tip of the pipette being gradually lowered so as to be always just beneath the surface of the liquid ; the portions were then transferred to small flasks. The apparatus was next removed from the thermostat and separated at the rubber band ; the ∪-tubes were wiped off outside with a dry cloth, the liquid on the inside adhering to the upper part of the middle arms also being removed ; and the tubes were weighed separately on a large balance, after adding to the anode portion a weighed amount of dilute nitric acid, sufficient to make the solution acid, thus avoiding later the absorption of carbon dioxide from the air. The contents of the ∪-tubes were now transferred as completely as possible to small flasks, the liquid being once poured back to secure thorough mixing. The ∪-tubes were then washed out, dried, and weighed. The flasks were all weighed, their contents poured out into the platinum dishes, and the nearly empty flasks again weighed. The weights of barium sulphate obtained from the cathode and anode portions were corrected for the small known weights of solution remaining in the ∪-tubes.

In the case of the potassium sulphate and barium chloride experiments, only the cathode and middle portions were analyzed. The method of conducting the electrolysis was also somewhat different in these cases. The side-arms of the ∪-tubes were at the beginning filled with solution for two-thirds of their length

(instead of up to a point only a little above the bends), and the concentrations of the acid and base solutions added were made 10 per cent. less (instead of greater) than would be required to maintain a constant concentration, in order to prevent the portions around the electrodes from sinking into the unchanged solution beneath. These solutions were added from burettes with tips turned upward and delivering a little below the bottom of the electrodes, which reached as before just beneath the surface of the liquid. The weight of the sulphuric or hydrochloric acid solution added was calculated from the measured number of cubic centimeters with the help of the known specific gravity of the solution ; this volume measurement is unobjectionable in the case of the acid solution added, since no non-volatile matter is introduced, and the greatest accuracy is therefore not required ; but direct weighing of the base solution is far preferable in case the anode portion is to be analyzed. Both methods of charging the U-tubes and of regulating the concentration at the electrodes give satisfactory results ; in that last described, the middle portion is of greater length, and the electrolysis could perhaps be longer continued, if it were desired to do so. The method used in the case of the barium nitrate is preferable, however, when the base solution to be added, like that of barium hydroxide, is heavy ; for, if the other method is used, it is difficult to prevent the added portions from sinking down before they become mixed with the liquid already surrounding the electrode. The electrolyses of the potassium sulphate and barium chloride solutions were continued from four to eight hours.

4. RESULTS OF THE TRANSFERENCE DETERMINATIONS.

The experimental data and the calculated transference numbers are given in the tables below. All the values given (except, of course, the current, time, and transference numbers) are weights in grams. Those in the columns relating to the salt content are the quantities of the substances actually weighed ; namely, of the potassium sulphate and barium sulphate. In the second column, the portion of the solution surrounding the cathode is designated by K, the adjoining middle portion by M_I, the next one by M_{II}, that adjoining the anode portion by M_{III}, and the anode portion itself by A.

The temperature was in all cases 25°.

The original solutions submitted to electrolysis, the concentrations of which are only approximately stated in the headings, were found to contain the following amounts of salt in 1,000 grams of solution : in experiments 1 and 2, 17.247 grams, in No. 3, 17.205 grams, and in Nos. 4, 5, and 6, 3.4927 grams K₂SO₄, in Nos. 7, 8, 9, and 10, 22.906 grams, in Nos. 11, 12, and 13, 4.6448 grams, in Nos. 14, 15, and 16, 21.083 grams, in No. 17, 21.099 grams, in Nos. 18 and 19, 4.6666 grams, and in No. 20, 4.6560 grams barium sulphate. The barium hydroxide solution added in experiments 14, 15, 16, and 17 gave 56.443 grams barium sulphate, and that used in experiments 18, 19, and 20 gave 11.700 grams barium sulphate for 1,000 grams of solution.

The values of the transference numbers, which are given in the last columns of the tables, are those of the positive ions multiplied by 100. The way in which these were calculated may be illustrated with the help of the data obtained in the first experiment with potassium sulphate (see the table below). The cathode portion submitted to analysis weighed 493.12 grams, and was found to contain 8.4394 grams potassium sulphate. To determine what it contained before the electrolysis, we must evidently subtract from the final weight of the portion, the weight of all matter which was introduced in the process of carrying out the electrolysis, and multiply the remainder by the original salt content, which was 0.017247 gram per gram of solution.

The weight of dilute sulphuric acid and phenolphthalein added, which was 60.78 grams in this experiment, must therefore be first subtracted. Secondly, a correction must be made for the fact that the weight of the cathode portion is, by the electrolysis itself, increased by the weight of the potassium ions which have migrated into it, and decreased by the weight of sulphate ions which have migrated out of it[1] by the weight of the hydrogen gas which escaped at the electrode. Since the average value of the transference number is found to be 0.493, the total increase of

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[1] It is evidently assumed hereby, as is always done in transference calculations, that the ions are not hydrated. It may not be without value to call attention to the fact that the commonly observed change of the calculated transference numbers with the concentration may be due, wholly or in part, in the case of concentrated solutions, to hydration of the ions, and to the failure to take this into account in the calculation.

weight from these three causes would evidently be : (39.1 ×
0.493)—(48.0 × 0.507)—1.0 = —6.0 grams for every 108 grams
of silver deposited in the voltameter, or —0.14 gram in this
experiment. The increase in the amount of the salt in the
cathode portion is therefore 8.4394—(493.12—60.78 + 0.14)
0.017247 = 0.9803 gram. Adding to this the change in the
adjoining portion (+0.0013 gram) and dividing by the equiva-
lent weight of potassium sulphate (87.18), and by the number of
equivalents of silver precipitated in the voltameter, the transfer-
ence number is found to be 0.4941. (The cases where the adjoin-
ing middle portion suffered a change in concentration greater
than the analytical error and where consequently this change was
combined with that of the cathode or anode portion, are indicated
in the table by a brace following the two quantities.) The cal-
culation of the transference number from the change in concen-
tration at the anode was, in the case of the barium nitrate experi-
ments, made in an entirely analogous manner, except that from the
weight of barium sulphate obtained from the anode portion after
the electrolysis, there was of course subtracted the amount com-
ing from the barium hydroxide solution added. For the sake of
greater clearness, the total weight of salt obtained from the anode
portion is in the table resolved into the two corresponding com-
ponents.

POTASSIUM SULPHATE, 0.1 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid or base solution added.	Original salt content.	ference in alt content.	Silver in voltameter. Current. Time.	Transference number.
1	K	493.12	8.4394	60.78	7.4591	+0.9803 }	2.4594	49.41
	M$_I$	137.47	2.3723		2.3710	+0.0013 }	0.118 amp	
	M$_{II}$	204.82	3.5365		3.5326	+0.0039	310 min	
2	K	456.48	7.7762	91.21	6.3033	+1.4729 }	3.6760	49.33
	M$_I$	175.15	3.0126		3.0209	—0.0083 }	0.134 amp	
	M$_{II}$	86.96	1.4993		1.4998	—0.0005	415 min	
3	K	434.79	7.4142	48.70	6.6446	+0.7696	1.9370	49.19
	M$_I$	119.85	2.0615		2.0620	—0.0005	0.063 amp	
	M$_{II}$	133.38	2.2941		2.2948	—0.0007	460 min	

POTASSIUM SULPHATE, 0.02 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid of base solution added.	Original salt content.	Difference in salt content.	Silver in voltameter. Current. Time.	Transference number.
4	K	491.47	1.6964	56.73	1.5185	+0.1779 ⎫	0.4451	49.68
	M$_I$	103.75	0.3631		0.3624	+0.0007 ⎬	0.028 amp	
	M$_{II}$	102.99	0.3599		0.3597	+0.0002·	240 min	
5	K	463.31	1.5869	84.31	1.3238	+0.2631 ⎫	0.6524	49.59
	M$_I$	176.04	0.6131		0.6149	−0.0018 ⎬	0.040 amp	
	M$_{II}$	94.08	0.3289		0.3286	+0.0003	245 min	
6	K	469.56	1.6246	57.40	1.4397	+0.1849	0.4617	49.58
	M$_I$	103.17	0.3604		0.3603	+0.0001	0.018 amp	
	M$_{II}$	107.24	0.3745		0.3746	−0.0001	380 min	

BARIUM CHLORIDE, 0.1 MOLAR.

7	K	460.04	10.6238	30.33	9.8402	+0.7836	1.7479	41.44
	M$_I$	46.30	1.0598		1.0605	−0.0007	0.108 amp	
	M$_{II}$	99.09	2.2686		2.2697	−0.0011	240 min	
8	K	512.08	11.9214	57.06	10.4182	+1.5032	3.3519	41.46
	M$_I$	35.77	0.8189		0.8193	−0.0004	0.122 amp	
	M$_{II}$	104.51	2.3911		2.3939	−0.0028	410 min	
	M$_{III}$	99.00	2.2673		2.2677	−0.0004		
9	K	507.37	11.7885	50.98	10.4500	+1.3385 ⎫	2.9804	41.48
	M$_I$	106.63	2.4411		2.4424	−0.0013 ⎬	0.123 amp	
	M$_{II}$	101.06	2.3116		2.3149	−0.0033	360 min	
	M$_{III}$	90.10	2.0615		2.0638	−0.0023		
10	K	474.93	10.8589	30.31	10.1824	+0.6765 ⎫	1.5019	41.50
	M$_I$	103.15	2.3604		2.3628	−0.0024 ⎬	0.065 amp	
	M$_{II}$	108.48	2.4821		2.4848	−0.0027	345 min	
	M$_{III}$	85.59	1.9574		1.9605	−0.0031		

BARIUM CHLORIDE, 0.02 MOLAR.

11	K	514.75	2.3897	54.95	2.1354	+0.2543 ⎫	0.5321	44.31
	M$_I$	110.70	0.5149		0.5142	+0.0007 ⎬	0.034 amp	
	M$_{II}$	115.31	0.5362		0.5356	+0.0006	230 min	
	M$_{III}$	89.89	0.4175		0.4175	0.0000		
12	K	499.37	2.3214	50.15	2.0864	+0.2350 ⎫	0.4928	44.19
	M$_I$	110.59	0.5142		0.5137	+0.0005 ⎬	0.022 amp	
	M$_{III}$[1]	86.12	0.4007		0.4000	+0.0007	275 min	
13	K	493.42	2.2930	49.84	2.0601	+0.2329 ⎫	0.4885	44.16
	M$_I$	106.63	0.4957		0.4953	+0.0004 ⎬	0.023 amp	
	M$_{II}$	109.52	0.5089		0.5087	+0.0002	260 min	
	M$_{III}$	95.84	0.4451		0.4452	−0.0001		

[1] Portion M$_{II}$ was lost in this experiment.

BARIUM NITRATE, 0.1 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid of base solution added.	Original salt content.	Difference in salt content.	Silver in voltameter. Current. Time.	Transference number.
14	K	244.30	5.2507	40.53	4.2970	+0.9537 ⎫	1.9334	45.54
	M$_I$	180.57	3.8058		3.8070	—0.0012 ⎬	0.175 amp	
	M$_{II}$	199.75	4.2106		4.2112	—0.0006	165 min	
	M$_{III}$	239.02	5.0368		5.0388	—0.0020 ⎫		
	A	205.23	⎰ 2.5491		3.5000	—0.9509 ⎭		45.56
			⎱ 2.2196	39.325				
15	K	269.42	5.8130	43.89	4.7562	+1.0568 ⎫	2.1540	45.47
	M$_I$	174.74	3.6864		3.6840	+0.0024 ⎬	0.178 amp	
	M$_{II}$	174.33	3.6760		3.6753	+0.0007	180 min	
	M$_{III}$	183.50	3.8710		3.8685	+0.0025 ⎫		
	A	218.25	⎰ 2.5877		3.6497	—1.0620 ⎭		45.48
			⎱ 2.5527	45.233				
16	K	268.51	5.7520	44.355	4.7270	+1.0250 ⎫	2.0917	45.46
	M$_I$	172.63	3.6428		3.6395	+0.0033 ⎬	0.173 amp	
	M$_{II}$	147.53	3.1110		3.1098	+0.0002	180 min	
	M$_{III}$	157.03	3.3132		3.3100	+0.0032 ⎫		
	A	204.41	⎰ 2.1725		3.2065	—1.0340 ⎭		45.56
			⎱ 2.9600	52.44				
17	K	278.03	5.8841	46.49	4.8846	+0.9995 ⎫	2.0301	45.54
	M$_I$	168.20	3.5492		3.5488	+0.0004 ⎬	0.168 amp	
	M$_{II}$	158.30	3.3329		3.3326	+0.0003	180 min	
	M$_{III}$	153.30	3.2360		3.2345	+0.0015 ⎫		
	A	205.69	⎰ 2.4465		3.4451	—0.9986 ⎭		45.42
			⎱ 2.3988	42.50				

BARIUM NITRATE, 0.02 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid of base solution added.	Original salt content.	Difference in salt content.	Silver in voltameter. Current. Time.	Transference number.
18	K	197.50	1.0234	20.88	0.8242	+0.1992	0.4042	45.57
	M$_I$	122.58	0.5744		0.5744	±0.0000	0.033 amp	
	M$_{II}$	134.06	0.6267		0.6269	—0.0002	180 min	
	M$_{III}$	187.20	0.8143		0.8150	—0.0007 ⎫		
	A	253.88	⎰ 0.7158		0.9149	—0.1991 ⎭		45.70
			⎱ 0.6766	57.83				
19	K	207.34	1.0631	21.75	0.8660	+0.1971	0.4014	45.41
	M$_I$	124.05	0.5773		0.5772	+0.0001	0.033 amp	
	M$_{II}$	141.65	0.6608		0.6610	—0.0002	180 min	
	M$_{III}$	145.38	0.6781		0.6772	+0.0009 ⎫		
	A	268.13	⎰ 0.7979		0.9971	—0.1992 ⎭		45.68
			⎱ 0.6371	54.45				
20	K	201.18	1.0346	21.14	0.8382	+0.1964	0.3985	45.57
	M$_I$	123.27	0.5630		0.5630	+0.0000	0.035 amp	
	M$_{II}$	121.00	0.5641		0.5640	+0.0001	170 min	
	M$_{III}$	155.48	0.7240		0.7239	+0.0001		
	A	279.26	⎰ 0.8353		1.0329	—0.1976		45.85
			⎱ 0.6716	57.40				

The values of the transference numbers obtained (multiplied by 100) are summarized in the following table. At the foot of each column are given the mean of the values just above, and the average deviation of the separate values from this mean. To the final results in the case of the barium nitrate, the probable error, calculated in the usual manner, is appended:

POTASSIUM SULPHATE.		BARIUM CHLORIDE.	
0.1 Molar.	0.02 Molar.	0.1 Molar.	0.02 Molar.
49.41	49.68	41.44	44.31
49.33	49.59	41.46	44.19
49.19	49.58	41.48	44.16
——-	·——	41.50	
49.31	49.62	——-	·——
0.08	0.04	41.47	44.22
		0.02	0.06

BARIUM NITRATE.

0.1 Molar		0.02 Molar.	
Cathode values.	Anode values.	Cathode values.	Anode values.
45.54	45.56	45.57	45.70
45.47	45.48	45.41	45.68
45.46	45.56	45.57	45.85
45.54	45.42		
——	——	——	——
45.50	45.50	45.52	45.74
0.04	0.06	0.07	0.07

45.50 ± 0.02   45.59 ± 0.10

5. ACCURACY OF THE RESULTS.

The probable degree of accuracy of the results and the consequent reliability and value of the method employed may be next considered. It should be first stated that in the above tables all the determinations are recorded which were carried to completion after certain errors which were found to exist in the analyses were eliminated.

In the cases of potassium sulphate and barium chloride, there are two indications of the degree of accuracy of the results; first, the change in weight of the middle portions, and second, the variations in the transference values calculated from the different experiments. In regard to the former, it should be stated that in the analyses of portions of the original solutions, variations from the mean salt-content of 0.0010 gram in the more concentrated, and of 0.0005 gram in the more dilute solution, were found

to exist ; so that only when the middle portions change by more than these amounts, do the changes have much significance. It will be seen that the changes in the M_I portions do not much exceed these amounts except in the cases of Experiments 2, 5, and 10 ; and in the first two of these experiments, the changes in the M_{II} portions are so small as to cause no hesitation in combining the changes of the M_I portions with those of the cathode portions. It will also be seen from the summary in the last table that the average deviation of the separate transference values from the mean is in every case less than 0.2 per cent. Taking into account the possibility of an error of 0.1 per cent. in the determination of the original salt content, it can, I think, be safely asserted that it is almost certain that the error in the mean transference values does not exceed 0.25 per cent. ; in other words, the third figure cannot be in error by more than one unit. The probable error is, of course, much less.

In the case of the barium nitrate experiments, a more conclusive confirmation of the degree of accuracy of the results is furnished by a comparison of the cathode and anode values ; for an error in the determination of the original salt content of the solution or any error arising from mechanical loss in the analysis of the portions would affect these values in the opposite direction. In the case of the 0.1 molar solutions, the agreement is complete between the mean cathode and anode values. Taking into account, moreover, the smallness of the variations of the separate values from the mean, and the slight changes (0.2–0.7 mg.) exhibited by the M_{II} portions, the final result (45.50) can, I believe, be regarded as almost surely accurate to 0.1 per cent. of its value. In the case of the 0.02 molar solution, the values calculated from the changes at the two electrodes differ by a little less than 0.5 per cent. Attributing double weight to the cathode results, since an increase of the salt content is produced by the base solution added at the anode, I adopt 45.59 as the most probable value. This may possibly be in error by 0.3 per cent., but is probably accurate to one-half that amount. Since, at both concentrations, the final values are derived by the combination of the results of two independent methods, which are liable to error in opposite directions, the probable errors given in the table are to be regarded as a measure not merely of the variable errors, but probably of all errors involved.

These considerations show that the degree of accuracy attained with the help of the method described in this article is much greater than that which it has heretofore been found possible to secure. This arises mainly from the fact that the electrolysis could be continued until a much larger weight of salt was transferred. Thus, in my experiments, the quantities transferred were 180–260 mg. in the 0.02 molar, 700–1500 mg. in the 0.1 molar solution, while, in Bein's determinations at corresponding concentrations, only 20–50 mg. were transferred.

6. COMPARISON WITH EARLIER RESULTS.

Potassium sulphate was investigated by Hittorf[1] at 4°–12° at two cóncentrations, at about 0.5 and about 0.014 molar. The transference numbers found were 0.500 and 0.498, respectively. The differences from my values (0.4931 and 0.4962) are, therefore, not very large.

Barium chloride has been studied by various investigators with widely divergent results. Thus Hittorf[2] obtained the value 0.385 at 10°–20° for 0.04–0.06 molar solutions, while from Bein's results,[3] one finds by interpolation for 25° and 0.1 and 0.02 molar concentrations, the values 0.424 and 0.445, respectively. The latter differ by 2.2 and by 0.7 per cent., respectively, from those presented in this article (0.4147 and 0.4422). Hopfgartner's[4] determinations (at 15°) for a 0.1 molar solution lead to the value 0.408, which is nearly as much below my result as Bein's is above it.

Barium nitrate has been investigated only by Hittorf,[5] who found 0.380 in 0.07, and 0.398 in 0.03 molar solution. These values differ very widely from my own (0.455).

These results make evident the great need of a repetition of much of the earlier work on tri-ionic salts.

7. CHANGE OF THE TRANSFERENCE NUMBERS WITH THE CONCENTRATION.

The effect of concentration, the study of which formed the main object of this investigation, may be now considered.

[1] Ostwald's Klassiker, No. 21, 58 ; or Pogg. *Ann.*, 98, 29–30.
[2] Ostwald's Klassiker, No. 23, 41 ; or Pogg. *Ann.*, 106, 380–381.
[3] *Ztschr. phys. Chem.*, 27, 51.
[4] *Ztschr. phys. Chem.*, 25, 138.
[5] Ostwald's Klassiker, No. 23, 41 ; or Pogg. *Ann.*, 106, 378–379.

The transference number of potassium sulphate varies only from 0.4931 to 0.4962, or about 0.6 per cent., between the concentrations of 0.1 and 0.02 mol per liter. A little consideration will show that this change can be explained by assuming that 1.2 per cent. more of the dissociated part of the salt is dissociated into $K^{•}$ and KSO_4' ions in the concentrated than in the dilute solution, it being further assumed, as a sufficiently close approximation, that the equivalent conductivities of all the ions involved are equal. But, since, according to Kohlrausch's measurements, the molecular conductivity between these two concentrations changes from 175 to 208 reciprocal ohms (and the dissociation from 64.5 to 77 per cent.) thus by 19 per cent., it is clear that by far the most important chemical change produced by the dilution is the dissociation of K_2SO_4 molecules and not KSO_4' ions. Since the change in the transference number is so small, it may, however, be due solely to the hydration of ions.[1] Therefore, only the following negative conclusion is justifiable : *The concentration of KSO_4' ions in a 0.1 molar potassium sulphate solution does not exceed a very few per cent. of the total concentration.* If these ions exist at all, they have a very much greater dissociation tendency than the neutral potassium sulphate molecules.

In the case of barium nitrate, the change (0.2 per cent.) caused by the fivefold dilution, is still smaller, and does not exceed the probable experimental error. Therefore, *barium nitrate solutions, up to a concentration of 0.1 mol. per liter, contain in appreciable quantity only $Ba^{••}$ and NO_3' ions and no complex ions formed by the combination of these.*

The difference in the transference numbers (0.4147 and 0.4422) of barium chloride at the two concentrations is very much greater than the differences just considered, amounting as it does to 6.6 per cent. The change is, moreover, in the opposite direction from that required by the assumption of the existence of $BaCl^{•}$ ions in the more concentrated solution. In order to explain this behavior and the analogous one of strontium and calcium chlorides, Bein assumed a partial hydrolysis of the salt, basing this view on the disagreement of a single determination of the amount of calcium transferred with determinations of the chlorine trans-

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[1] Thus the actual change of 0.6 per cent. would be entirely accounted for, if with the equivalent weight of the $K^{•}$ ions migrate two molecules of water more than migrate with the equivalent weight of SO_4'' ions.

ferred.   This explanation cannot, however, be correct, since the
alkaline earth hydroxides are known to be very strong bases ; it
is, moreover, entirely disproved in the case of barium chloride, by
the substantial agreement (see § 6) of Bein's values, which are
based on determinations of the chlorine transferred, with my
results which were obtained by determining the transferred
barium.   On the contrary, the behavior of these chlorides of the
alkaline earth metals is entirely similar to that of the halogen
compounds of cadmium, though the anomaly is less pronounced ;
and as far as I am able to see, it admits only of a corresponding
explanation.   In order to account for the fact that the sum of
the transference numbers for the metal and chlorine is equal to
unity, and for the change with the dilution, it is, namely, neces-
sary to assume that *there are present in considerable quantity in
the 0.1 molar solution of the alkaline earth chlorides, complex nega-
tive ions formed by the union of one or more chlorine ions with one or
more of the chloride molecules* (such ions for examples as $BaCl_3'$ or
$BaCl_4''$) and that these ions dissociate with increasing dilution.

8. RATES OF MIGRATION OF THE BIVALENT IONS.

As Kohlrausch has pointed out, owing to the lack of exact
transference values for tri-ionic salts, the Law of the Independent
Migration of the ions has not been satisfactorily confirmed in the
case of bivalent ions, nor have their rates of migration, calcula-
ted with the help of that law, been as accurately determined as
have those of univalent ions for the reason just mentioned, and
also for the reason that the limiting value of the molecular con-
ductivity of tri-ionic salts cannot be established with as great cer-
tainty, since a larger extrapolation is necessary.

With the help of the new transference numbers for potassium
sulphate and barium nitrate, the equivalent conductivities of the
SO_4'' and Ba'' ions can be calculated if it be assumed that the
values obtained for 0.02 molar solution at 25° would also hold
true for extreme dilution and at 18°.   That these assumptions
will not give rise to an error greater than 1 per cent. is highly
probable in view of the small changes between the concentrations
of 0.1 and 0.02 mol per liter, and in view of the general principle that
temperature has, as a rule, only a small effect on transference
numbers.   The calculation can be made in two ways, either by

combining with my transference numbers the conductivities at
extreme dilution of the $K^{\cdot}$ and NO_3' ions, which have been
derived by Kohlrausch through a consideration of the transfer-
ence numbers and the molecular conductivities of the di-ionic
salts; or by combining with them the limiting values of the
equivalent conductivities of potassium sulphate and barium
nitrate. The results so obtained for the SO_4'' and $Ba^{\cdot\cdot}$ ions can
be then further compared with Kohlrausch's values which were
derived by a combination of the two kinds of data last mentioned,
without reference to the transference number of any tri-ionic salt.[1]

The three pairs of calculated values of the equivalent conduc-
tivities of the two ions are given below in the order in which they
have just been referred to. The data used in the calculation are
the transference numbers recorded above (0.4962 for K_2SO_4 and
0.4559 for $Ba(NO_3)_2$) and the following values of the equivalent
conductivity expressed in reciprocal ohms at extreme dilution[2]:
for $K^{\cdot}$, 64.8; for NO_3', 61.3; for K_2SO_4, 135.5; and for
$Ba(NO_3)$, 119.3.

	I.	II.	III.
SO_4''	65.8	68.3	69.7
$Ba^{\cdot\cdot}$	51.4	54.4	57.3

The differences between the three pairs of values are by no
means inconsiderable. In the case of the $Ba^{\cdot\cdot}$ ion, indeed, the
first and third methods of calculation give results differing by
over 10 per cent. Aside from serious errors in the experimental
data, these differences may be due to one or more of the three
following causes: first, error in the conductivity values calcula-
ted for the univalent ions; second, error in the extrapolated
values for the equivalent conductivity at extreme dilution of the
tri-ionic salts; and third, inaccuracy in the assumption that the
transference numbers for potassium sulphate and barium nitrate
at extreme dilution do not differ much from those found in 0.02
and 0.1 molar solution. It seems very improbable that any one
of these three errors can be large enough to account for the diver-
gences; a combination of them, however, may possibly do so.
In the absence of definite information in regard to the matter, it
seems best to adopt provisionally the values given in column II

[1] Wied. *Ann.*, 66, 805.
[2] These values are those given by Kohlrausch, Wied. *Ann.*, 66, 795 and 819, 812 and 804.

($SO_4'' = 68.3$; $Ba'' = 54.4$) which are the ones most directly derived from experimental data, and which are not far from the means of the other two pairs of values. These numbers give for the equivalent conductivities of potassium sulphate and barium nitrate, 133.1 and 115.7, respectively, while Kohlrausch's extrapolated values are 135.5 and 119.3. In this connection it should be pointed out that in Kohlrausch's method of treatment of tri-ionic salts, the assumption involved that the conductivity of bivalent ions decreases with increasing concentration more rapidly than that of the univalent ions simultaneously present, is entirely inconsistent with the transference results on potassium sulphate and barium nitrate presented in this article. This is shown by the following transference numbers which are calculated for these two salts from his values for the separate ions at the various normal concentrations which are stated below in the head line :

	0.1	0.05	0.02	0.01	0.001
K_2SO_4	0.571	0.557	0.534	0.522	0.499
$Ba(NO_3)_2$	0.397	0.414	0.434	0.446	0.468

It is certain from my results that any such change of the transference numbers with the concentration is out of the question in the case of these two salts. It ought to be added that Kohlrausch regarded his assumption only as a provisional one, having an empirical justification. That the results obtained with its help were at all satisfactory is probably due, first to the fact that the compounds considered were mostly those of the halogens, and secondly, to the large errors in some of the transference numbers.

It is impossible to utilize the transference numbers of barium chloride, as was done with those of the nitrate, for the calculation of the conductivity of the barium ion, since the transference number of the former salt does change greatly with the dilution. It is of interest, however, to make the converse calculation so as to compare the transference number calculated for extreme dilution with that found at the concentrations investigated. Assuming as above, $Ba'' = 54.4$, and according to Kohlrausch, $Cl' = 66.4$, the transference number for complete dissociation is found to be 0.450. (Even assuming Kohlrausch's much higher value (57.3) for the Ba'' ion, the transference number becomes only 0.464.) The value found for a 0.02 molar solution was 0.442, so that the change produced by further dilution is relatively small.

At this concentration, therefore, the complex negative ions present in considerable quantity in more concentrated barium chloride solutions are, for the most part, dissociated.

In closing, I desire to state that the accuracy of the experimental results presented in this article are to be attributed in large measure to the analytical skill and perseverance of my assistants, Mr. A. A. Blanchard and Mr. G. V. Sammet.

IMPROVEMENT IN ORSAT APPARATUS.

BY A. BEMENT.

HAVING experienced considerable trouble in using the Orsat gas apparatus, I have devised a modification with the object of removing what I have found to be a serious and troublesome fault.

Fig. 1 will illustrate the particular difficulty in question. It is that of the usual form of pipette used especially for the caustic and pyrogallate reagents, having a number of small glass tubes

Fig 1.   Fig. 2.   Fig. 3.
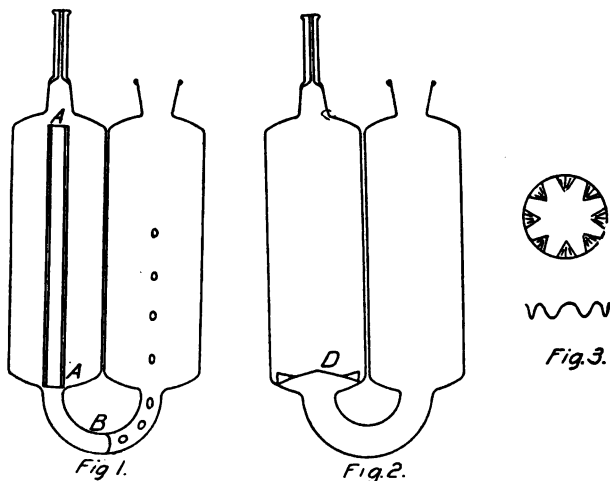
inclosed in the front leg. For purpose of illustration only one of these tubes is shown by AA. As this chamber in practice is full of these tubes, it necessarily follows that one of them must

be in the center, and this one may, and often does, drop down in the position indicated in the sketch. The result is that a direct passage from A down through the tube and into the branch B is produced, and at the same time, the outlet from the other tubes and the remainder of the chamber is stopped off, leaving the outlet for the reagent only by way of this center tube, because by its junction at lower A, a close connection is made. The result is, that as gas enters the pipette the reagent instead of uniformly receding before it is driven down the center tube, and this condition may exist to such an extent that the reagent is driven to the point B, when the gas, owing to its lower gravity, will bubble up through the reagent, as shown, and escape to the atmosphere. It does not always follow that this center tube will make as close a junction as shown, but the trouble exists to a greater or less degree in all instruments. I have found cases where it required a period of fifteen minutes to pass the gas sample into the pipette, and have known of frequent errors caused by a loss of gas from this cause. It is, of course, true that if sufficient time be taken, the gas may be worked into the pipette without loss, but it is certainly desirable and important that the analysis be effected with as little trouble as possible, and in the shortest time consistent with careful work. It may be observed when gas is passed into the pipette that the reagent does not recede equally before it, but that contained in the center tube may drop down lower than the surface in the other tubes. Likewise, when the gas is withdrawn the reagent returns in greater volume by way of the center tube, and will rise higher and run over the top.

To overcome this difficulty, I have devised the pipette shown in Fig. 2, which prevents the tubes dropping down into the outlet by interposing a glass disk with corrugated edge, as shown in Fig. 3. This not only affords a support but allows a free passage of larger area from each tube to the connecting branch, as the depressed edges of the disk rest on the bottom of the pipette chamber, leaving ample passage between the corrugations. The connecting passage may also be made larger, thereby affording opportunity for the quick passage of the reagent, and shortening the time required for absorption.

CHICAGO, October 18, 1900.

REVIEW.

Participants of the convention were :

Prof. Dr. A. Herzfeld, chairman.

Prof. Dr. Brodhun, delegate of the Imperial Physical-Technical Institute, Berlin.

Regierungsrat Dr. von Buchka, delegate of the Imperial Institute of Hygiene, Berlin.

Mr. Camuset, chairman of the Technical Commission of the Syndicate of French Sugar Manufacturers.'

Dr. Hermann, of the laboratory of Dr. Alberti and Hempel, Hamburg.

Mr. François Herles, trade-chemist, Prague.

Mr. A. Jobin, Paris.

Mr. François Sachs, Brussels.

Mr. Saillard, chemist of the Chambre Syndicale des Fabricants de Sucre, France.

Regierungsrat F. Strohmer, delegate of the Association for the Beet-Sugar Industry in Austria-Hungary.

Mr. van Voss, chairman of the Association of Dutch Sugar-Manufacturers.

Dr. Otto Wendel, of the laboratory of Dr. Hugo Schulz, Magdeburg.

Dr. F. G. Wiechmann, delegate of the American Sugar Refining Company, New York.

Dr. H. W. Wiley, chief chemist, Department of Agriculture, Washington, D. C.

Dr. Heinrich Winter, Java.

The chairman opened the session on July 24, 1900, in the large hall of the Chambre Syndicale des Fabricants de Sucre de France, welcomed those present and expressed special thanks ·to the Chambre Syndicale des Fabricants de Sucre de France for the hospitable reception as well as for having delegated Mons. Camuset to the meeting of the commission.

Messrs. Bunge, Kiew, Van Ekenstein, Amsterdam, Nevolé, Prague, and Dupont, Paris, requested that their absence be excused.

After the chairman had given a short résumé of the origin, as well as of the prior work of the commission, he requested Messrs. Saillard and Wiechmann to again undertake the editing of the French and the English text of the Proceedings, which both gentlemen willingly agreed to do.,

Referring to the prior written communication, the chairman then once more put before the commission the question: Which normal weight should be valid for the German instruments, when using the metric flask? As is well known, the Imperial Physical-Technical Institute has called attention, by its communication dated October 19, 1898, to the fact, that an exact conversion of the normal weight 26.048 grams for Mohr's cubic centimeters at 17.5° C., corresponds to 26.01 grams (not 26.00), metric volume, at 20° C., determined in air, with brass weights.

"The Commission decides that, in consideration of the insignificance of the deviation, the normal weight of 26.00 grams shall henceforth be adopted for 100 metric cubic centimeters, at 20° C., determined in air with brass weights."

Mr. Wiley then spoke of the results of his researches concerning the influence of temperature on the polarization of sugar; his remarks are given in the *Vereins-zeitschrift*.

This was followed by a communication by Mr. Wiechmann, of New York, concerning the influence of temperature on the specific rotation of sugar, an abstract of his publication appearing in the *Zeitschrift des Vereins der Deutschen Zucker-industrie*.

A long discussion bearing on the substance of the two lectures followed, in which Professor Dr. Brodhun removed some wrong conceptions which some of those present had entertained, concerning the experimental basis of the lectures, and especially concerning the researches which the Imperial Physical-Technical Institute at Berlin had made on the same subject.

Mr. Pellat was unable to be present on the day of the session; the commission therefore agreed to be present at his lecture, Friday, July 27, 1900, in the session of Section V, of the Congress for Applied Chemistry, as Mr. Pellat intended to give his lecture on the day and at the place named.

Mr. Jobin reported that he himself had not made personal investigations regarding the influence of temperature on polariscopic instruments; he referred solely to his earlier publication on this subject, as well as to the coming lecture of Mr. Pellat. Mr. Jobin discussed the errors with which instruments provided with quartz-wedge compensations are burdened; this gave rise to a longer discussion.

Then Professor Dr. Herzfeld made a brief report on the results of the examination of quartz plates, concerning which a full report will be found in the *Vereins-zeitschrift*. The commission agrees that these quartz plates shall be divided among the nations represented; for the United States, the quartz plates are to be sent to the Department of Agriculture, at Washington; for France, to the syndicate of the sugar manufacturers; for Belgium, Holland, Austria-Hungary, and Russia, to the associations of

sugar manufacturers which are represented in the session by delegates.

The session was then adjourned for lunch, and reopened at 2 o'clock in the afternoon of the same day.

AFTERNOON SESSION.

Herr Regierungsrat Strohmer delivered his lecture on a uniform method of sugar analysis for international trade, and submitted, as a basis for the same, the agreement which the Austro-Hungarian chemists had last reached in their convention, June 22, 1896, at Budapest. Mr. Strohmer proposed to accept these resolutions, with certain deviations, as a basis of the international agreement, and suggested for this purpose the separate discussion of the different topics. The convention agreed to do this, but first of all considered it necessary to establish general principles for the adjustment of polariscopic instruments, as well as for the avoidance of errors caused by the influence of temperature.

On motion of Messrs. Camuset and Saillard, first of all, the following was adopted:

"*The convention declares it to be necessary that the rotation of chemically pure sugar be accepted as the fundamental basis in saccharimetry.*"

The chemically pure sugar which is to be employed for this purpose shall everywhere be prepared according to the same method, which is as follows (method of the English chemists):

Purest commercial sugar is to be further purified in the following manner: A hot saturated aqueous solution is prepared and the sugar precipitated with absolute ethyl alcohol; the sugar is carefully spun in a small, centrifugal machine and washed in the latter with some alcohol. The sugar thus obtained is redissolved in water, again the saturated solution is precipitated with alcohol and spun and washed as above. The product of the second centrifugaling is dried between blotting-paper and preserved in glass vessels for use. The moisture still contained in the sugar is determined and taken into account when weighing the sugar which is to be used.

The convention furthermore decided that central stations shall be designated in each country which are to be charged with the preparation and the distribution of chemically pure sugar. Wherever this arrangement is not feasible, quartz plates, the values of which have been determined by means of chemically pure sugar, shall serve for the control of the saccharimeters.

Mention should be made of the fact that in the discussion on this topic, it was remarked, on the one hand, that the preparation of chemically pure sugar is not an easy task, and that in countries

having hot climates, sugar is dried with difficulty and hence is not stable, and hardly available for transportation. Thereupon it was pointed out that the above control, by means of chemically pure sugar, should, as a rule, apply only to the central stations which are to test the correctness of saccharimeters ; for those who execute commercial analyses, the repeated control of the instruments is to be accomplished, now as before, by means of quartz plates.

Concerning the working temperature the following resolution of Mr. François Sachs was unanimously adopted :

" In general, all sugar tests shall be made at 20° C.

"The adjustment of the saccharimeter shall be made at 20° C.; one dissolves for instruments arranged for the German normal weight, 26 grams of pure sugar in a 100 metric cubic centimeters flask,[1] weighing to be made in air, with brass weights, and polarizes the solution in a room, the temperature of which is also 20° C.; under these conditions, the instrument must indicate exactly 100.00.

"The temperature of all sugar solutions to be tested is always to be kept at 20° C., while they are being prepared, and while they are being polarized.

" However, for those countries, the temperature of which is generally higher, it is permissible that the saccharimeters be adjusted at 30°C. (or at any other suitable temperature) under the conditions specified above and providing that the analyses of sugar be made at that same temperature."

Objections were raised against the universal normal weight, 20.00 grams, by Mr. François Sachs as well as·by Mr. Strohmer. In consequence, it was resolved not to undertake the introduction of the same, but to adopt the resolution :

The general international introduction of a uniform normal weight is desirable.

It was furthermore resolved, on the basis of the proposition of Mr. Strohmer, *to observe the following rules in raw sugar analysis.*

I. POLARIZATION.

'' In effecting the polarization of substances containing sugar, half-shade instruments only are to be employed.

'' During the observation, the apparatus must be in a fixed, unchangeable position, and so far removed from the source of light that the polarizing Nicol is not warmed by the same.

'' As source of light there are to be recommended, lamps with intense flame (gas triple burner, with metallic cylinder, lens, and reflector ; gas lamp, with Auer burner ; electric lamp ; petroleum duplex lamp ; sodium light).

[1] Or during the period of transition 26.048 grams in 100 Mohr's cubic centimeters.

"The chemist must satisfy himself, before and after the observation, of the correctness of the apparatus (by means of correct quartz plates), and in regard to the constancy of the light; he must also satisfy himself as to the correctness of the weights, of the polarization flasks, the observation tubes, and the cover glasses. (Scratched cover glasses must not be used.)

"Several readings are to be made and the mean thereof taken, but any one individual reading must not be selected.

POLARIZATION OF RAW SUGAR.

"To make a polarization, the whole normal weight for 100 cubic centimeters is to be used, or a multiple thereof for any corresponding volume.

"As clarifying and decolorizing reagents there may be used: sub-acetate of lead, prepared according to the 'Pharm. Germ.' (three parts by weight of acetate of lead, one part by weight of oxide of lead, ten parts by weight of water), Scheibler's alumina cream, concentrated solution of alum. Boneblack and decolorizing powders are to be absolutely excluded.

"After bringing the solution exactly to the mark, and after wiping out the neck of the flask with filter-paper, all of the well shaken, clarified sugar solution is poured upon a dry, rapidly filtering filter. The first portions of the filtrate are to be thrown away, and the balance, which must be perfectly clear, is to be used for polarization.

WATER.

"In normal beet-sugars the water determination is to be made at 105° to 110° C.

"For abnormal beet-sugars, as well as for colonial sugars, there is no commercial method for the determination of water.

ASH.

"To determine the ash-content in raw sugars, the determination is to be made according to Scheibler's method employing pure concentrated sulphuric acid. For an ash-determination, at least 3 grams of the sample are to be used. The incineration is to be carried out in platinum dishes, by means of platinum or clay muffles, at the lowest possible temperature (not above 750° C.).

"From the weight of the sulphate-ash thus obtained, 10 per cent. are to be deducted, and the ash-content, thus corrected, is to be recorded in the certificate.

ALKALINITY.

"As, according to the most recent investigations, the alkalinity of raw sugars is not always a criterion of their durability, the

commission abstains from proposing definite directions for the
execution of these investigations.

INVERT SUGAR.

"The quantitative determination of invert sugar in raw sugars is
to be made according to the method of Dr. A. Herzfeld
(*Zeitschrift des Vereins für die Rübenzuckerindustrie des Deutschen
Reiches, 1886, pp. 6 and 7*)."

Furthermore the following resolutions were adopted:

" The commission declares that only well-closed glass vessels
will insure the stability of samples.

" To obtain correct results it is desirable that the samples con-
tain at least 200 grams of material."

All of the above resolutions were adopted *unanimously* by those
present.

The chairman then declared that he considered the work of
the commission completed, and he requested the convention to
authorize him to prepare and to accept the protocol, and there-
upon to declare the commission dissolved.

Mr. Wiley, however, stated that he considered it necessary
that the commission be made a permanent one. He proposed
that Mr. Herzfeld be again elected chairman. This resolution
was unanimously carried.

After Mr. Wiechmann had expressed the thanks of those
assembled, to the chairman, the session was closed.

FRIDAY, JULY 27, 1900.

The members of the commission, in accordance with the
resolutions adopted on Tuesday forenoon, attended the session of
Section V, of the International Congress for Applied Chemistry,
and there heard the lecture of Mr. Pellat on the " Influence of
Temperature on the Specific Rotation of Sugar."

F. G. WIECHMANN, *Secretary*.

NOTE.

Estimation of Fat in Sweetened Condensed Milk.—In the
Journal for October, 1900, appears an article by J. F. Geisler,
on " The Estimation of Fat in Sweetened Condensed Milk," in
which reference is made to " A Method of Analysis for Canned
Condensed Milk "[1] wherein the results are stated to be " so
utterly out of harmony with the composition of commercial con-
densed milk, etc.," that I feel it only proper to call attention to
the eight determinations obtained by my critic in extracting the

[1] This Journal 21, 439 (1899).

fat with petroleum ether, and " ether-petroleum ether "—results ranging from 8.31 to 8.468 per cent. which, while approaching some of my own results, are still somewhat lower than might be expected after the painstaking methods of extraction.

As to the statement that, " In the writer's experience, it is the rare exception rather than the rule, for condensed milks to contain less than a proportion of 25 per cent. of fat in the milk solids," it would seem that such experience is not exactly in harmony with some of the recognized authorities ; for it is only necessary to refer to the article by T. H. Pearmain and C. G. Moor[1] where several analyses are given in which the fat is less than 2 per cent. of the whole, or less than 7 per cent. of the milk solids.

Moreover, the highest result, 8.468 per cent. fat, as given in the article by J. F. Geisler; would be by calculation 25 per cent. of 33.87 per cent. milk solids,—a result decidedly lower than the usual percentage of milk solids in condensed milk, judging from the published analyses of Leffmann and Beam, T. H. Pearmain and C. G. Moor.

Hence the possibility, in view of the omission to state the total solids and cane-sugar, that my critic may have proved the rare exception in his experience by obtaining fat proportionately less than 25 per cent. of the milk solids.

I have taken this opportunity to make the above statements, because of the criticism offered, before the general meeting of the Society in June, when I was unable to attend.

<div align="right">FREDERIC S. HYDE.</div>

NEW BOOKS.

VICTOR VON RICHTER'S TEXT BOOK OF INORGANIC CHEMISTRY. EDITED BY PROF. H. KLINGER. AUTHORIZED TRANSLATION, BY EDGAR F. SMITH. Assisted by WALTER T. TAGGART. Fifth American, from the tenth German edition, carefully revised and corrected. Philadelphia: P. Blakiston's Son & Co. 1900. xii + 430 pp. Price, $1.75.

The recent edition of von Richter's inorganic chemistry, translated by Professor Smith sustains the reputation of former editions in containing a large amount of subject-matter in a limited space, and in presenting the most recent additions to the

[1] *Analyst*, **20**, 268.

knowledge of this subject. The arrangement of the present
edition is based on the periodic system of Mendelejeff and Lothar
Meyer, and it presents a logical sequence of fact and theory
according to the inductive method. The book is considerably
enlarged from former editions by the introduction of chapters on
the periodic law, relations of chemical affinity, and a brief state-
ment of the theories of solubility and thermochemical phenomena.
These are useful additions since training in elementary chemistry
cannot now be considered complete unless these recent concep-
tions of chemical theory receive some attention.

The introduction seems a little heavy for a beginner, but for
the best use with beginners as with any good text-book much
depends on the skill and faithfulness of the teacher. For rapid
advance, it is essential that the student gain a clear idea as to
what chemistry is before proceeding to the study of facts and
phenomena. Doubtless this is best accomplished by a brief pre-
liminary statement of elementary principles, illustrated by experi-
ments to be performed by the student.

This edition appears at an opportune moment, and it will
doubtless meet with the favor it deserves.

                                        CHARLES F. MABERY.

THE ELEMENTS OF PHYSICS. BY HENRY CREW. Second edition. xvi +
    353 pp. New York: The Macmillan Company. 1900. Price, bound, $1.10.

In the preface to the first edition, the author said : '' Physics
is not a series of disconnected subjects, including mechanics,
sound, light, heat, and electricity. It is, on the contrary, a body
of well-organized truth, forming one great whole. * * * A
science covering fields apparently so diverse, yet so intimately
connected, demands an elementary treatment which shall be
rigidly consecutive.''

The more importatnt changes from the first edition are the
following : '' All use of the method of limits, either for defining
physical quantities or for other purposes, has been abandoned.
All Greek letters, except π, have been replaced by English
symbols. All use of trigonometrical functions has been given
up.''

These changes are good ones from the point of view of the
teacher of physics. On the other hand, the student would
certainly find his calculus come easier if he saw from the start

the advantage of the differential notation. A bright boy sees at once that algebra is an improvement over arithmetic, but he does not see the advantages of the calculus at the time when he is studying the subject. It seems as though the teacher of physics might with profit, present his subject so that the student would feel the need of more advanced mathematics. This, however, is a debatable question, and the author has the argument of experience on his side. His book is certainly a good one.

WILDER D. BANCROFT.

L'EAU DANS L'INDUSTRIE. PAR H. DE LA COUX. Paris. V Ch. Dunod, Editeur. 49 Quai des Grands-Augustins. 1900. Price, 15 francs.

As the name "water in the industry" (or industrial arts) indicates, this work by M. De la Coux, a chemical engineer and professor of industrial chemistry for the Polytechnic Association in Paris, takes up the several questions connected with the utilization of water, natural and acquired impurities, and the means for removing the same, and lastly the methods of testing and analysis. The scheme of treatment is reasonably comprehensive, and in some portions is very adequately and fully developed, and in others, not so completely as in other works already available.

The distinctive characters and differences of composition of the various classes of natural waters are first stated, and the solubility of certain salts in water considered from the industrial point of view ; as for example, the effects on the boiling of water.

The next section on the use of water in boilers and for the raising of steam, the difficulties from the development of incrustation and so-called "boiler-scale," the remedies and means of removal of incrustations, both mechanical and chemical, is very full and satisfactory in its treatment. Not only are the several chemical salts which have proved of value as scale-removing materials discussed separately, but the calculations given by which (the extent of the impurity in the water being known) the amount of correction needed may be ascertained. The means of purifying mine waters and salt water to make them available for boiler purposes is also very thoroughly covered.

The employment of water in special industries is then noted and the requirements and conditions of purity in each discussed. Thus, the use of water in the textile and tinctorial industries, in

tanning, in the preparation of tanning and dye-wood extracts, in paper-making, in sugar refining, in brewing and distilling, in ice manufacture and for alimentary preparations are all referred to, and the special requirements stated.

The question of the general purification of water by chemical treatment, by filtration and sterilization is also treated, although somewhat from the standpoint of French methods and with very little mention of the experimental work done in England and Germany.

The treatment and purification of waste waters from various industrial operations is then discussed, mention being made specially of the waste-waters from beet-sugar refineries, from dye works, and from works yielding soapy or greasy residual waters. The recovery of glycerine from the soap-maker's waste lyes is also referred to. This section is, however, not so broadly conceived or handled as is done in König's well-known work : " Die Verunreinigung der Gewässer, deren schädlichen Folgen, sowie die Reinigung von Trink and Schmutz wasser," the second edition of which appeared last year in two volumes.

The chemical analysis of water, both qualitative and quantitative, forms the subject of the last section of the work and is reasonably full, although not comparable with books like Tiemann-Gärtner, and special American works on this branch.

The book, however, in the compass of 496 pages, covers a wide range of topics and on the whole, quite satisfactorily.

<div align="right">SAMUEL P. SADTLER.</div>

BOOKS RECEIVED.

The Protection of Shade Trees in Towns and Cities. Bulletin No. 131, Connecticut Agricultural Experiment Station, New Haven, Conn. November, 1900. 30 pp., with numerous plates.

Report of the Connecticut Agricultural Experiment Station, for the Year ending October 31, 1900. Part I.—Fertilizers. New Haven, Conn. 112 pp.

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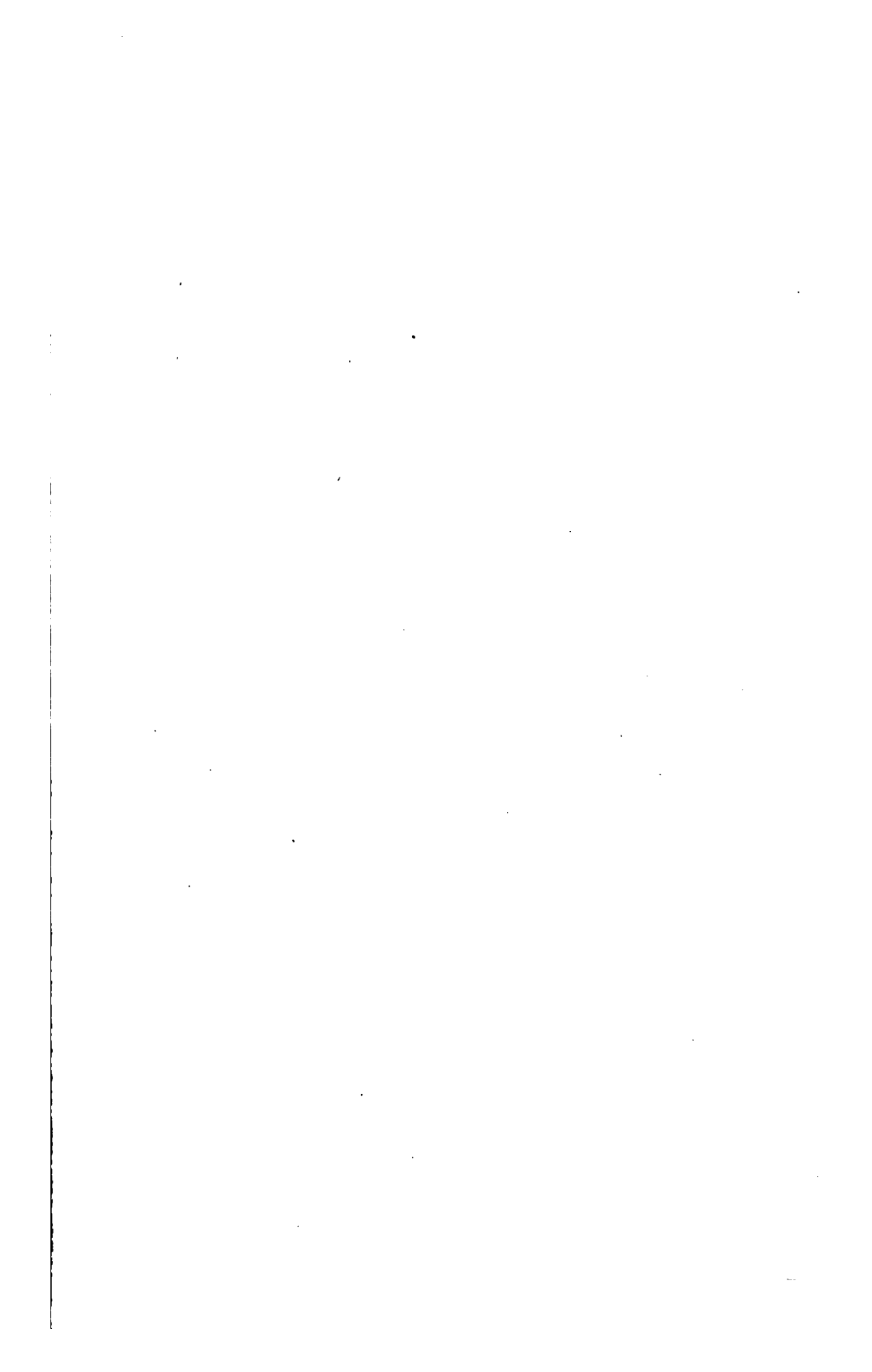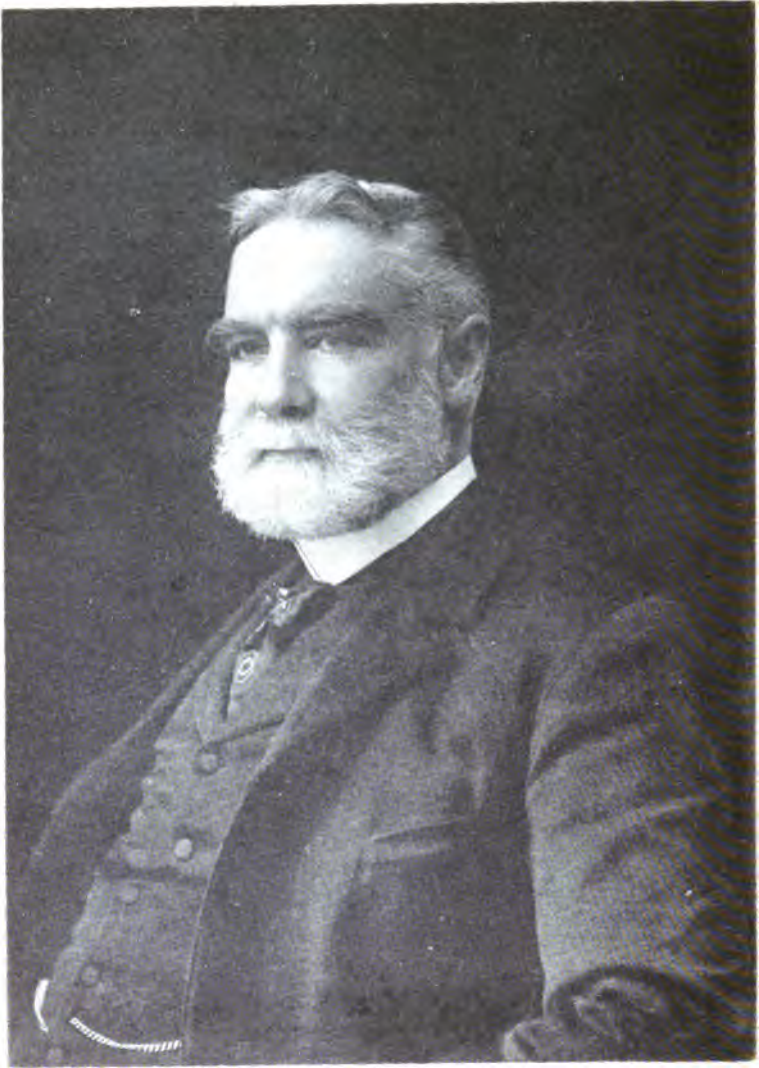
Yours very Cordially

Wm McGlurstrie

THE JOURNAL

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AMERICAN CHEMICAL SOCIETY.

THE CONDITION, PROSPECTS, AND FUTURE EDUCA-TIONAL DEMANDS OF THE CHEMICAL INDUSTRIES.[1]

By Wm. McMurtrie.

IT has been well said that chemistry is an offspring of the nine-teenth century. The closing years of the eighteenth century had some glimpses of the wonders the new science had in store, but it remained for the workers of the first decade of the nineteenth to collaborate the results obtained by their immediate predecessors and develop the new truths which finally established the foundation of the glorious structure, which has now grown so great. During this period, human necessities were in every way augmented and particularly in France, claimed to be the father-land of our science, human ingenuity was sorely taxed to meet these needs.

The struggle to find ways and means stimulated the energies and increased the zeal of the searchers after truth, and the utili-tarian quest, as is always inevitable, brought forth results of interest and value above and beyond the actual needs, furnished data upon which are based the most important and fundamental laws of the science, and firmly established many of the most important of our industries. The labors of the chemists of the

last decade of the closing century had cleared away the haze
which surrounded and covered the truths already developed and
opened the way for further promotion of the newly born science.
Lavoisier had led by the introduction of systematic and accurate
observation and record, to the crystallization of what had so far
concentrated, and his associates, imbued with his spirit and
inspired by his genius, were ready and willing to carry forward
what he had so nobly begun.

And so the science was launched. How it has progressed dur-
ing the century now closing has been told in many ways by many
men and the history seems ever new. New laws and new truths
found applications in the industries and increased the material
wealth and the industries in turn furnished the material, the
data, the incentive, for much of the additional investigation
necessary to the development of the further laws.

The activity of the last decade of the last century has its coun-
terpart in that of the century just closing. If the former century
established the foundations, the closing century has furnished a
superstructure worthy of the great minds who began the work.
And whether we consider the later achievements from the side of
abstract science or from that of the applications of the great laws
to the material needs the glory is equally manifest and the won-
der no less profound. Whether we consider argon and helium,
neon, krypton, and xenon, and the beautiful researches which led
to their discovery, polonium and radium, and their remarkable
properties, the Roentgen reactions or the liquefied gases, and the
attainment of the almost lowest limit of low temperatures, or the
wonderful advances in illumination, the production of high tem-
peratures in the electric furnace, the development of new com-
pounds and forms of matter through the aid of these tempera-
tures, the applications of high electric tensions to the production
of new reactions, even those most familiar with them must feel
the influence of the mighty strides and look into the future with
enthusiastic hope.

The interest manifested in the new science in the old world was
quickly extended to the new and it found most active lodgment
here. Students and associates of Black in Scotland, Fothergill
in England, and of the French chemists of the last quarter of the
century in Paris, started the work and the names of Rush, Hutch-

inson, Woodhouse, McLean, Franklin, Rumford, Priestley, Silliman, Hare, Seybert, Norton, Dana, and others, will ever find affectionate memories in the minds of the chemists of America. What these men started has been actively developed by those who followed them, until to-day the science and its applications find more actual workers in our country than is to be found in any other country within the bounds of civilization.

The first half of the century had comparatively few men in the United States who could be classed as working chemists. Chemistry had, it is true, been taught in a way in many of the colleges. But systematic work, as we know it to-day in many of the institutions of learning, was practically unknown. Those who felt the special need of, and had a desire for, such instruction, were constrained to seek the facilities in other lands, until generous and at the same time practical men, such as Lawrence, Sheffield, Packer, Pardee, and Harrison, with enterprising eyes and prophetic vision, saw the advantages to be derived from the further development of the sciences and provided the means whereby well furnished laboratories could be opened up and facilities for the profound study of the science could be made possible. But the industrial needs of the country for more exact knowledge of the natural laws extended beyond private munificence and the national legislatures early recognized the importance of the better education of those who must manage the rapidly growing industries. The successful efforts of the late Senator Justin S. Morrill and his associates in securing the enactment of the law, which provided for the establishment in each state of an institution for study of agriculture and the mechanic arts, is well known and will always be gratefully remembered. No less important were the efforts of the late Mr. Hatch, of Missouri, who labored so earnestly and eventually so successfully for the establishment of the state agricultural experiment stations. There can be no question that nothing has done more for the promotion of the science of chemistry and its applications than the acts of these great captains of industry and legislation. We shall not forget further the wonderful benefactions of Johns Hopkins, Clark, Case, Rose, Rockefeller, Stanford, Schermerhorn, Havemeyer, Fayerweather, Carnegie, and others, who have furnished, through splendid

munificence, the magnificent facilities not only for instruction in the science but for abstract research as well.

The science received splendid impulse and inspiration in the meeting at the grave of Priestley, in 1874. It brought the chemists of the country, then comparatively few in number, together and established the bond of good fellowship and scientific sympathy, always so necessary to true progress. The most important outcome of this most important gathering was the organization of our own Society. In his address delivered at that meeting, Professor Benjamin Silliman named 85 chemists who had contributed to the advancement of the science in the United States at that time.

In 1876, the American Chemical Society was organized and during the year enrolled 230 members, of whom 190 were professional chemists. The impulse given in Northumberland was effective, the example of a few devoted and public-spirited men was followed, and though a period of almost fifteen years was requisite to the ultimate firm establishment of the work of the organization and the integrity of the Society itself, the great aims of its founders to secure the harmonious and thorough organization of all the chemists of the country finally prevailed. The Society has continued to increase in membership and influence, until at the present time thirteen local sections have been established in various parts of the country all actively working, and at least six of them holding monthly meetings during all but the summer months, for such scientific intercourse and discussion as cannot fail to be fruitful in the promotion of the science. The roll of membership now contains about 1750 names and while this represents but a small proportion of the working chemists of the country, its growth henceforward must be rapid and the hope of the founders fairly realized.

The Journal covers, annually, nearly 1000 pages of matter fairly representative of the work of American chemists and it has become necessary because of increased demands for it to publish an edition of 2700 copies. Its pages are open to communications on all subjects relating to chemistry and its applications, and it is the hope and expectation that the valuable Review of American Chemical Research may be accompanied in the near future by abstracts of papers published in the foreign journals, thus furnish-

ing to all our members information regarding the world's work in chemical science and practice.

The progress made in the applications of chemistry in our country can properly and fully be told only in the results of the census now in progress and in hands which promise results of higher value than have ever before been obtained in such work in this country. We may congratulate ourselves that it has been entrusted to our past president, Dr. C. E. Munroe, whose tastes and training have so admirably fitted him for the delicate and difficult task submitted to him. But we have in the figures prepared by the Bureau of Statistics of the United States Treasury most significant data regarding the progress made during this closing decade of the closing century. From this source we learn that of products classified as chemicals, drugs, and medicines, we imported during the year ending June 30, 1890, to the value of $41,601,978, while for the year ending June 30, 1900 this value had become $52,931,055. Most of the materials represented in these figures entered into consumption in industries, based wholly or in part upon the applications of chemistry. We cannot enter into the details of these statistics, but we may consider with interest and profit a few figures relating to some well-known industries and which are instructive in this connection, as showing the variations which have occurred during the decade.

CHEMICALS IMPORTED IN 1890 AND 1900 RESPECTIVELY :

	1890.	1900.
Caustic soda	$1,470,335	$ 158,793
Soda ash....................	3,493,288	665,104
Potash, chlorate of	238,840	102,337
Soda, chlorate of............	......	93,076
Lime, chloride of	1,385,080	1,461,858
Glycerine	928,935	2,138,670
Alizarine colors.............	358,882	771,336
Coal-tar colors and dyes	1,787,553	4,792,103
Other coal-tar products	....	397,780
Milk, sugar of	46,510	399
Glass......................	7,411,343	4,038,753

The figures indicate enormous growth of the alkali industry in the United States during the decade and show that in this branch of industry we are entirely independent as regards supplies of foreign producers. The figures for glycerine show the possibilities

of expansion of another industry, while the almost astounding growth of the importations of alizarine and coal-tar products and dyes indicate the necessity for the further development and utilization of our own sources of crude materials of like character and the extension of that already begun. The rapid growth of the establishment of the by-product coke ovens reveals great possibilities in this direction and it must be disappointing if the characteristic enterprise fails to take advantage of these possibilities.

If the importations of chemical products are interesting and indicate great activity and growth in the industry, the figures for the exportation of similar products are even more significant. We submit figures for the years ending June 30, 1890 and June 30, 1900 respectively, including in the table some data for 1876, the year of the organization of our Society. To have predicted these results in the beginning of the quarter century would have invited incredulity, but so also would predictions regarding the advances to be made in other lines of human industry. The figures are worthy of careful study.

VALUES OF EXPORTS OF DOMESTIC PRODUCTS OF THE CHEMICAL INDUSTRIES FOR THE YEARS ENDING JUNE 30, 1876, JUNE 30, 1890, AND JUNE 30, 1900 RESPECTIVELY :

	1876.	1890.	1900.
Bark and extracts for tanning ...... $	223,276	$ 263,754	$ 376,742
Beeswax	......	17,927	91,913
Blacking	81,401	238,391	880,049
Candles	229,311	143,073	191,687
Celluloid	......	39,004	174,264
Acids	50,300	98,084	146,722
Ashes, pot and pearl.............	75,597	26,211	49,566
Copper, sulphate of	......	......	2,120,745
Dyes and dyestuffs...............	......	717,128	498,056
Lime, acetate of	......	......	776,413
Other chemicals not separately enumerated	2,471,195	2,840,931	5,536,716
Cider	......	193,283	64,283
Coke............................	......	53,586	1,233,921
Coffee and cocoa, ground and prepared, and chocolate	......	93,735	228,241
Earthen-, stone-, and chinaware ...	......	175,477	575,823
Fertilizers	922,221	1,618,681	7,218,224
Glass and glassware..............	646,954	882,677	1,933,201
Glucose or grape-sugar...........	......	855,176	3,600,139
Glue	5,798	88,484	225,844

	1876.	1890.	1900.
Grease, grease scraps, and soap stock	......	1,506,819	2,944,322
Gunpowder and other explosives...	67,887	868,728	1,888,741
India rubber, gutta percha, and manufactures of...............	88,816	1,090,367	2,364,157
Ink, printers' and other...........	......	147,057	259,776
Leather	......	11,175,141	15,363,584
Lime } Cement }	77,568	134,994	{ 85,854 { 163,162
Malt	......	60,412	215,198
Malt liquors	42,664	654,408	2,137,527
Matches...........................	153,680	52,284	95,316
Naval stores	9,799,923	7,444,446	12,474,194
Oil cake and oil cake meal	.... .	7,999,926	16,757,519
Oils, animal	1,975,972	1,686,643	718,997
" mineral, crude...............	2,220,268	6,744,235	7,364,162
" " refined or manufactured........................	30,502,312	51,403,089	68,246,949
" vegetable, corn	......	......	1,351,867
" " cotton-seed	146,135	5,291,178	14,127,538
" " linseed	23,770	55,036	54,148
" volatile or essential	248,270	223,435	256,597
" all other	......	102,792	554,295
Paints, pigments, and colors.......	179,882	578,103	1,902,958
Paper and manufactures of	795,176	1,226,686	6,215,559
Paraffin and paraffin wax	......	2,408,709	8,602,723
Perfumery and cosmetics..........	375,011	430,151	*358,589
Photographic materials	......	3,891	1,164,465
Plaster	......	5,153	35,017
Lard..............................	22,429,485	33,455,520	41,939,157
Lard compound and substitutes....	......	......	1,474,464
Oleo and oleomargarine	......	6,773,522	10,920,400
Butter............................	1,109,496	4,187,489	3,142,378
Cheese	12,270,083	8,591,042	4,939,255
Milk	......	303,325	1,133,296
Salt..............................	18,378	29,073	55,833
Soap..............................	684,739	1,109,017	1,773,921
Spermaceti........................	35,915	116,757	67,125
Spirits, wood.....................	......	......	320,306
" grain (neutral and cologne)	......	178,257	59,277
" brandy	......	......	83,698
" rum	......	663,039	903,808
" whiskey, bourbon..........	......	498,250	764,860
" " rye	......	137,029	121,241
" all other	......	165,535	24,921
Starch	524,596	378,115	2,604,362

* 1899.

	1876.	1890.	1900.
Sugar and molasses	6,745,771	3,029,413	3,697,366
Tallow	6,734,378	5,242,158	4,398,204
Varnish	54,906	206,483	620,059
Vinegar	6,133	10,520	12,583
Wine	33,483	270,930	62,592
Wood pulp	......	2,245	458,463
Yeast	......	.....	36,061
	102,054,750	174,803,105	264,501,771

The figures show grand totals as follows :

For the year 1876	$102,054,750
" " " 1890	174,803,105
" " " 1900	264,501,771

In the decennial period just closing, the increase in the value of the exports of products of domestic manufacture was therefore about the same as during the preceding fourteen years, and during the quarter century the growth has been 260 per cent. The growth has been persistent and steady and indicates what may be expected in the immediate future as well as what is now the condition of development of our chemical industries. This latter condition becomes more manifest when we consider that the products exported constitute but a small proportion of the production, and we may in some degree at least anticipate the results which must be obtained in the pending census investigation.

As further illustration of the growth of the chemical industries, we may call attention to the condition of the coke industry in the United States in 1880 and 1898, respectively, as illustrated in the following table :

	1880.	1898.
Establishments	186	342
Ovens { built	12,372	48,447
{ building	1,159	1,048
Coal used, net tons	,5,237,471	25,249,570
Coke produced, net tons	3,338,300	16,047,299
Total value of coke at ovens	$6,631,267	$25,586,699
Value of coke at ovens, per net ton	$1.99	$1.594
Yield of coal in coke, per cent	63.0	63.6

If we consider that in the recovery ovens, which are fast taking the places of the older and less rational types, this coal should yield 3.38 per cent. of tar, 0.34 per cent. its weight of ammonia and 8.17 per cent. of gas liquor, all of them bases of most important chemical industries, the figures are significant.

Equally interesting must be the information to be furnished regarding the capital represented in the chemical industries in this country. At the present time, we are able to judge of this to a minor extent from the reported capitalization of the recently organized companies constituting combinations of preexisting companies. It is true that in these cases the capital represents in a very considerable measure what is known as good will, franchises, etc., but it nevertheless represents earning power and the average market value corresponds very closely with par value. Taking only those organizations devoted to the chemical manufactures exclusive of the gas and metallurgical and explosive industries, we find that the capitalization as reported in the stock lists amounts to the enormous value of about $1,500,000,000 and this takes no account of many of the incorporated industries not specially reported, nor the industries not incorporated and yet active. It does not include the recently developed electrolytic industries, in which the cash capital actually invested, as we learn from competent authority, amounts to more than $1,500,000. The newly established by-product coke industry is rapidly developing and is absorbing capital with wonderful rapidity, while the comparatively new beet-root sugar industry has already developed to such an extent as to involve capitalization of nearly $100,000,000 and to develop the establishment of manufacturing plants of magnitude beyond the imagination of foreign manufacturers in the same line a few years ago. Yet this is a general characteristic of the modern chemical industries of the United States and it is interesting to note that much of the development has been effected empirically and by men comparatively little versed in the principles and laws of the science upon which they are based. The industries have had the aid of but few educated chemists. Happily this condition is rapidly changing. Rational work is coming to be recognized and the demand for well-trained chemists is increasing. We cannot yet boast with the Germans that single works employ more than 100 thoroughly educated chemists, yet inquiry shows that many of the important works have corps of chemists numbering from 10 to 50, while very many more have smaller numbers. The same inquiry affords some clue to the number of chemists actually at work in this country. If we compare the list of members of the American

Chemical Society, we find that more than two-thirds are engaged
in technical work.   Furthermore, of the few chemists reported in
the inquiry just referred to, scarcely one-third are members of the
Society.   A fair estimate based upon such data leads to the con-
clusion that more than 5,000 chemists are actually at work in the
United States, and that 80 per cent. of these are connected with
the industries.   A study of the lists of the graduates of the edu-
cational institutions leads to similar conclusions.   Fischer reported
as the result of special inquiry made three years ago that in Ger-
many 4,000 graduate chemists were employed in the industries
and about 200 in teaching and special investigations.

So then we find that the chemical industries 'of the United
States are growing with enormous rapidity ; that they are being
concentrated into fewer but larger works; that operations and
reactions are being carried out with a magnitude which the earlier
chemists would never have predicted; that new methods are being
followed ; new principles applied, greater accuracy of results
demanded both as to quality and yield of the products ; that the
products now issue from the works in lots of tons at a time of a
higher degree of purity and with a greater economy than was
possible but a few years ago with lots of a few hundred pounds.
For instance, the great sugar refineries each yield from 1,000,000
to 2,000,000 pounds daily of a product, the purity of which may
be considered absolute.   The modern beet-sugar works have in
some cases capacity for treatment of from 1,000 to 3,000 tons of
roots daily and consequently the purification of almost an equal
quantity of juice.

And if so great advance has been made during the closing
quarter century and even decade, what shall we say of the possi-
bilities of the future?   What is to be the magnitude of the chem-
ical industries of the United States?   What shall be the character
of the products issuing from them?   What will they require of
the men who must direct and control them?   That is to say, what
will be the educational requirements of the American chemical
industries of the almost immediate future?   These questions are
not new to our own country and their importance has forced itself
with powerful intensity upon those engaged in the chemical
industries in the old world ; it has been the subject of most ear-
nest discussion, particularly in Germany and England, during

the past five years at least. Nor has it been in all respects satis-
factorily answered. Even within this closing month of the clo-
sing century the cable has flashed news of the complaint on the part
of the leading statesmen of England that the training of technol-
ogists in that country is inadequate to the development necessary
to meet foreign competition and at]almost the same time brings
news of the inauguration of new institutions for technical educa-
tion. And in Germany also, the home and starting-point of
many of the great industries, the demands upon the educational
institutions for the better training of technologists are being
pressed from every side. It is natural to believe that the time is
not far distant when we too shall be called upon to make and
meet similar demands. It may be pardonable therefore to discuss
briefly what these requirements are likely to be.

First of all, experience shows that those who financially con-
trol the great industries, fully appreciate the need of improvement
in both processes and products, are particularly apt in propound-
ing hard questions in connection therewith and always expect
that these questions shall be answered quickly and with the
utmost accuracy. Young men who early come to a realization of
this fact and prepare themselves by broad and thorough education
to meet it are those who will succeed in the industries and ulti-
mately have a controlling influence in their management. And
what is to be said here on this subject is directed as much to the
students as to those who instruct, for it is not difficult to under-
stand the restrictions placed upon teachers by the students them-
selves, in the struggle to arrange work leading to the training,
which many realize to be absolutely essential to meet the require-
ments of the near future.

For it is beyond question that the most thoroughly educated
man is sure to best meet these requirements and become the leader
in the industrial struggle of the near future. Dr. Duisberg, the
director of the great color works at Elberfeld, Germany, rightly
fixed the standard when he said that " above all a general com-
prehensive education is required. We must have in the indus-
tries persevering, energetic men with broad views." And Dr.
Chittenden was right when he said: "Given a young man of broad
knowledge and a thorough conception of the principal laws of
physics, mechanics, hydraulics, etc., and he will soon adjust him-

self to the environment of professional work, and eventually rise to a plane far beyond that of the man whose training has been purely technical," and concluding his paper he says: "The rapid development of the sciences and their manifold industrial applications have opened up avenues for new ventures of great magnitude and there is an increasing demand for young men of broad scientific knowledge and training. He who wishes for the fullest possible measure of success must prepare himself thoroughly for his life work and he can do this in no better way than by acquiring a broad and liberal education."

This important requisite to success could not be better described. Careful general training is conducive to the best thought and the best expression of the results of inquiry. And it is too frequently true that technical men are especially lacking in this particular. Too early specialization must tend to narrowness of view, and therefore to limited influence. The general culture work of the preparatory schools or of the colleges will always be profitable, whether as preparatory to a specialty or an auxiliary to its prosecution. These principles will apply to all technologists whether they are chemists or not.

But what shall be the character of the special training of the technical chemist? First of all, we must admit, that this must cover thoroughly and proroundly a study of the science of *chemistry*. Dr. Fittig declares: "Our problem is to study the science as such ; to lead the student into the methods of strictly scientific investigation, to put him into position to solve pure scientific problems entirely independent of the question, whether he shall devote his powers to the service of the science itself or apply it to practical questions." He claims that many students take up the study without the scientific instinct. And Erlenmeyer says: "A true scientific training should produce ability and susceptibility for all and every use. With a knowledge of the principles and laws of the science, their use becomes easy, they proceed independently." Foerster, discussing the needs of the electrochemists, says: "But above all be particular to secure fundamental training in the entire field of chemistry, thus utilizing the principle insisted upon by Liebig, that the best training for any specialty rests upon the broadest foundation in the whole of scientific chemistry." Dr. Duisberg says further: "In technical chem-

istry the sharp eye of the scientifically trained man is wanted in order to recognize the individual developments of the reactions in progress, which can be seen only through the accompanying indications." And Richard Meyer truthfully declared: "If our technologists did not properly appreciate the service rendered by men trained in the spirit of Liebig, chemical investigation would miss the stately crowd of auxiliary powers, without which the heights from which we may now look proudly backward and hopefully forward, could never have been attained." And W. H. Perkin says that "technical education will be of small value unless it is carried out on a very broad and scientific basis."

These views of the leaders in the science of chemistry must find an echo in the mind of every man who has had experience in the industries. In no department of human activity is a thorough knowledge of the fundamental laws so needful, nor can the knowledge of any law be safely neglected if successful work is to prevail. For all the laws apply all the time and few cases will arise in which the more important can be avoided. To suppose that the industries can be carried on in the face of severe competition without such knowledge is to invite failure in every case. Empiricism may succeed in times of plenty, but adversity breeds rationalism and fosters the support it can bring. So then we may make no distinction between inorganic and organic chemistry, analytic and physical chemistry, for each one has its place in the world's work, and no one can predict when any one of these branches will be called upon to render material aid.

But whatever may be the department of chemical study the relation of the science to physics will be keenly felt, and the dependence of each upon mathematics as the true foundation will become manifest. For this latter science is just as powerful an aid in the determination of the motions of the atom and molecule in matter as those of the worlds and constellations in space. And if it cannot be neglected in astronomy, no more can it in chemistry and physics. Indeed, it illustrates the unity of all the sciences, even as it does the correlation of all the forces. Dr. Lorenz set forth the need of all chemists in this particular when he said: "Modern electrochemistry is an exact science, and its principles, and a knowledge of it rests upon a foundation of mathematics. It is in every way desirable that every electro-

chemist shall be trained in the higher mathematics, and be thoroughly able to utilize both differential and integral calculus."
He particularly recommends as a preparation therefor the "Introduction to the Mathematical Treatment of the Sciences" of Nernst and Schönflies and says: "If the student have an intensive rather than extensive training in mathematics, he may be thrown into the sea of natural science and left to swim." So also Foerster discussing the character of the instruction in electrochemistry in the technical high school, while insisting upon " thorough fundamental work in inorganic and organic chemistry, physics and physical chemistry" does not fail to include in his plan of work " the principles of higher mathematics." Dr. Koerner, discussing the importance of physical chemistry to the industries, says: " It is most characteristic of it (physical chemistry) that it utilizes the most powerful of all natural aids to scientific investigation, the higher mathematics." And in the curricula of the technical high schools in Germany we find almost without exception that in the course of chemistry, as well as in engineering, the higher mathematics is taken up and completed before the end of the first year, if not before the end of the first semester. It thus becomes the ground-work of and preparatory to, all the important work, which in those great institutions must follow it.

And finally, the technical chemist of the near future must be trained in the principles and practices of engineering, trained to make and operate the mechanical means for carrying out effectively the chemical reactions of the industries in a large way. For after all these reactions differ only in degree from those of the research and preparation laboratories, and if in the latter the students must be trained in making and assembling the forms of apparatus for use in the various operations of pulverizing, separating, roasting and incineration, solution, precipitation, separation of solids and liquids, washing, drying, and care of precipitates and crystals, the production and control of heat, the transfer of solids and liquids, the production and application of vacuum, evaporation and distillation, the conditions of crystallization, etc.; in the small way in the laboratories, he must be taught to apply all these and more, in the large way in the works. Indeed, the only difference between the two may be comprised in the terms microchemistry and macrochemistry ; chemistry and the opera-

tions belonging to chemistry carried on in a small way with limited or small quantities or volumes ; handling solids and liquids in quantities of a few grams or a few cubic centimeters or liters on the one hand, or of tons of solids and thousands of gallons of liquid on the other. How, for instance, would the chemist, untrained in the principles of engineering, proceed in handling materials in quantities involving several tons of solid matters and 30,000 to 50,000 gallons of liquid in a single charge, a requirement not uncommon in the modern industries and sure to be more common in the future industry. In his day, perhaps, the great Liebig was right, and Wöhler was right, and Fittig, not far wrong, when they maintained that with a thorough knowledge of the principles and laws of chemistry, all else in the industry involving their application would be easy. It is possible that the genius of the young operator would come to his aid and enable him ultimately to devise means to meet his ends, but time and labor must be saved by training in the methods, whereby such means may be established and a knowledge of means already at hand acquired. The authoress of a late popular work of fiction was right when she said " untrained genius is a terrible waste of power," and though it may not be as applicable here as in an earlier paragraph, she was also right when she said in the same connection, "So many persons think that if they have a spark of genius, they can do without culture ; while really it is because they have a spark of genius that they ought to be and are worthy to be cultivated to the highest point." And this applies to the chemists who must operate in a large way and with large masses of matter, either solid or liquid.

In a discussion of this subject in England, where perhaps more than elsewhere in the world the need of engineering capacity on the part of chemists has been most keenly felt, and where on the other hand engineering capacity embodied in such men as. Mond, Bell Muspratt, Weldon, Perkin, and Chance, has brought forth such splendid results, Ivan Levinstein, himself, a leader in the industry, said : " It must also be palpable that a chemist intended for industrial work, who, along with sound training in chemistry, has also acquired a fair knowledge of chemical engineering, must be better fitted for his work than the man who is only practically acquainted with the handling of china basins, phials, or a Liebig's

condenser. And in the same discussion Watson Smith endorsed "what had been said as to the importance of teaching the scientific principles involved in the special construction of apparatus and plant for chemical processes on a large scale."

Dr. Ost, whose connection both with the industries and teaching, has been so intimate, says : "Liebig, who had for long years taught technical chemistry in Giessen and, as none other, had promoted the applications of chemistry, could say, in 1840, ' I know many (those trained in pure science only) who now stand at the head of soda, sulphuric acid, sugar and cyanide works, dyeing and other industries, and without ever having had previously to do with them, were completely entrusted with works' processes within the first half hour, and in the next brought forth a number of most important improvements.' Sixty years ago, this judgment characteristic of the time, this enthusiastic declaration of Liebig, would constitute a dogma, but it is no longer tenable. The chemist graduated from the technical high school is no longer in position to begin his factory experience with introduction of improvements." This, Ost says, is because of the better and more perfect organization of modern works. And Dr. Lorenz, of the Zurich Polytechnicum, says : "The electrochemist should not be graduated until he has been taught how to use modern methods in very large apparatus. We find in electrochemistry a wide difference between the theory and the facts. In the laboratory, current yield and greatest economy of electrical energy are often the principal considerations, but in technology corrosion of electrodes or diaphragms is much more expensive than any variation of energy." What an important illustration of a special study of materials of engineering in the preparation for the chemical industry ! And what a sensation of sympathy this must arouse in all those who have had to do with the handling of corrosive materials in the very large quantities and volumes, which modern methods involve ! How often it happens that success of an important operation is delayed and even made impracticable because of want of knowledge of suitable resistant material for construction of containing vessels or apparatus. Probably the most important contribution to this subject is that of Mr. Beilby. In his address he says : "I have rarely seen the chemistry of a process lagging behind the engineering ; most frequently it is the

other way. The chemical reactions involved in the ammonia soda process are simple and easily understood, but it required the genius and practical skill of men like Solvay and Mond to devise apparatus which could establish the manufacture on its present secure basis. What are the elements of which the skill is made up? The scientific basis must be a thorough knowledge of the principles of chemistry, physics, dynamics, and mechanics, and added to this there must be a practical acquaintance with the materials of construction and the methods by which they are worked into structures. The designing and construction of apparatus for chemical works is a distinct branch of applied science. It is in this that special skill is required, for works' operations are not simply laboratory operations. The ideal chemical engineer should be in thorough sympathy with the modes of thought and with the methods of working of both the chemist and the engineer; just as the professor of engineering teaches how to apply the laws of statics, dynamics, and kinematics to the design of structures or machines, so should the professor of chemical engineering trace the applications of the laws of chemistry and physics and dynamics in the problems which occur in designing chemical apparatus for works. I am quite satisfied that in the present state of popular opinion the position and work of the technical chemist will not be properly recognized, unless he can associate himself, by his training and practice with the engineering side of his calling." Prof. Meldola says : "The sooner a chemist is made to realize the enormous practical difference between a laboratory and a factory process, the better it will be for him."

Prof. J. A. Reynolds, Director of the Municipal Technical Schools of Manchester, England, says : "English chemists are not engineers and English engineers are not chemists, and hence the enormous difficulty which arises in the endeavor to bring to successful commercial results the fruits of laboratory research." While Mr. David Howard considers that "the influence of mass action, the question of so many pounds of coal per horse power hour, and other like things, cannot be dealt with on a small scale, but are all important on a larger scale. We want chemical engineers who can make new roads in chemistry, as mechanical engineers do in railways."

It is also important to consider the course of study proposed by Mr. Beilby in his paper for prospective industrial chemists. His large experience in the chemical industry gives him power to speak with authority, and young men who look forward to a successful career in the industry, will do well to give it most careful consideration. And even more important, perhaps, are the courses of instruction carried out in the West of Scotland Technical College and in the Municipal Technical School in Manchester, England, and published in the Journal of the Society of Chemical Industry during 1899. Students who have had the advantage of these courses must be better fitted than those who have not been similarly favored. Yet we must believe that the courses laid out in the technical high schools of Germany and, we are proud to say, in some of the schools of technology in our own country, are in some respects better. Yet a combination of the two courses might be made with profit to both classes of institution. It is important that the works' chemists should be trained in the construction of the special forms of apparatus he needs to use, but they should be accompanied or preceded by the principles and practice of mechanical engineering. The most practical courses, perhaps, are those laid down in many of our own educational institutions for instruction in mining engineering and metallurgy, in which chemistry of the operations is considered in connection with the mechanical details of its applications, and we have advised students desiring to prepare for the chemical industries to pursue these courses in the best institutions first, and to follow them with a year or more of exclusive study of chemistry both pure and applied. If it were possible to add to the courses of chemistry as much of engineering, civil, mechanical and architectural, as is found in some of the metallurgical courses, the ideal would be more nearly met. But we can fully sympathize with those teachers who find the time available too limited for such a combination, and appreciate the fact that either the student must come to the professional school with better preliminary training in the preparatory subjects, or the courses must be extended beyond the usually provided four years' work. In any case, if a course of engineering could be carried side by side, and simultaneously with the course of chemistry, the needs of the prospective technical chemist would be

most fully met, and the requirements of the future chemical industry most nearly fulfilled. In some of our institutions in which all studies are practically optional, such a course might be arranged and profitably followed, and notwithstanding the longer time which might be involved in its completion, the graduate from it would issue with brighter and better prospects of success in his profession than one less broadly trained. And in the selection of the subjects for such a course, the plans of study laid down in the technical high schools of Germany, in the technical schools of England, and of our own country, may be profitably followed.

In 1897, we expressed the view which seems thoroughly applicable now and which will perhaps bear repetition here. We said: "It seems therefore that the demand of the present time, and of the immediate future can be met only by broadly educated men: by men who have been trained, not only in chemistry itself, but in the great principles of physics as well. A good technical chemist must be first of all a thoroughly educated chemist; after that, to attain the highest success in this country, he must be educated in the principles of engineering; the productions and applications of heat; the productions and applications of electricity; the transmission of power, the movement of liquids; in general, the means whereby the reactions of chemistry may be carried out in a large way. We need, therefore, chemical engineers and these in the nature of the requirements must be broadly and thoroughly educated men. While they must be trained in the work of the research laboratories, which are being organized in connection with many of the great industries, they must likewise be prepared to put into practical operation in a large way the results of the researches they have been called upon to make."

These truths have not changed, and if these conditions of education and training are fully met, the progress of our chemical industries must be greatly augmented, the science, must, by reaction, be actively advanced, and following the experience of our German confrères in the words of Meyer, we may look hopefully forward and in the near future proudly backward, to accomplishments greater than the world has ever known.

EIGHTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1900.

BY F. W. CLARKE.

D URING the year 1900, fewer new determinations of atomic weight than usual, have appeared. The data are given in the following pages, together with Herzfeld's research upon calcium, which appeared three years ago. It was unfortunately published through an unusual channel, and was therefore overlooked at the time. Attention may also be called to the presidential address[1] of Professor Morley before the American Chemical Society, which is a valuable discussion of the probable accuracy of our knowledge as to the ratio between hydrogen and oxygen.

NITROGEN.

Dean's research[2] upon the atomic weight of nitrogen, which was noticed in abstract in the report for 1899, has now appeared in full. Weighed quantities of silver cyanide were dissolved in nitric acid, and the nitrate solutions were titrated with a standard solution of potassium bromide. As the latter was not absolutely pure its silver value was independently determined, and the titrations give therefore the quantity of silver proportional to the cyanide. The last experiment of the series was made by solution of the cyanide in sulphuric acid instead of the nitric acid previously used. Attempts to reduce silver cyanide in hydrogen gave unsatisfactory results, due to the formation of paracyanogen and silver carbide. The final data are subjoined.

	Weight AgCN.	Weight Ag.	Equivalent of CN.
	6.2671	5.0490	26.039
	17.60585	14.18496	26.026
	17.1049	13.7801	26.049
	17.9210	14.43881	26.030
	12.11215	9.75875	26.028
	14.6672	11.81727	26.029
Sum,	85.67820	69.02889	26.032

1 This Journal, 22, 51.
2 J. Chem. Soc., 77, 117.

If $C = 12.001$, then $N = 14.031$, the value finally adopted. All weights were reduced to a vacuum standard.

Another determination of the atomic weight of nitrogen has also been announced by Scott.[1] From ammonium bromide he finds $NH_4Br = 97.996$. For the chloride, $NH_4Cl = 53.516$. The first value is lower than that found by Stas, the second is in agreement with Stas. The full paper will appear early in 1901.

CALCIUM.

The following determinations by Herzfeld,[2] made in 1897, were overlooked at the time, and are now recorded here for the sake of completeness. Calcium carbonate was prepared from the bicarbonate, and reduced to oxide by ignition at a temperature of from 1300° to 1400°

Weight $CaCO_3$.	Weight CO_2.	Weight CaO.	Atomic weight Ca.
3.9772	1.7504	2.2268	39.687
2.3614	1.0396	1.3218	39.655
3.2966	1.4510	1.8456	39.677
			Mean, 39.673

Calculated with $H = 1$, $C = 11.92$, $O = 15.879$. With $O = 16$, $Ca = 39.975$.

IRON.

The determinations by Richards and Baxter[3] of the atomic weight of iron are based upon the reduction of pure Fe_2O_3 in a current of electrolytic hydrogen. Two series of results are given, representing ferric oxide prepared by two distinct methods. For details of manipulation the original paper must be consulted.

First Series.—Ferric oxide obtained by calcination of ferric hydroxide :

Weight Fe_2O_3.	Weight Fe.	Atomic weight Fe.
3.17485	2.22096	55.885
3.61235	2.52750	55.916
		Mean, 55.900

Second Series.—Ferric oxide obtained by calcination of ferric nitrate :

[1] *Proc. Chem. Soc.*, **16**, 205.
[2] *Ztschr. des Vereins für die Rübenzucker-Industrie*, **47**, Heft 497.
[3] *Ztschr. anorg. Chem.*, **23**, 245.

Weight Fe₂O₃.	Weight Fe.	Atomic weight Fe.
3.97557	2.78115	55.883
4.89655	3.42558	55.891
4.35955	3.04990	55.891
7.14115	4.99533	55.870
6.42021	4.49130	55.882
		Mean, 55.882

Mean of all seven determinations, 55.89, when $O = 16$. With $H = 1$, $Fe = 55.47$. All weights were reduced to a vacuum.

GADOLINIUM.

Atomic weight determined by Benedicks,[1] by synthesis of the sulphate from the oxide. Data as follows :

Weight oxide.	Weight sulphate.	Atomic weight gadolinium.
0.4308	0.7171	156.57
0.5675	0.9451	156.35
0.5726	0.9534	156.44
0.6785	1.1301	156.29
0.7399	1.2329	156.10
1.3253	2.2063	156.52
		Mean, 156.38

Calculated with $O = 16$, and $S = 32$. The final result agrees well with the determination by Bettendorf, who found $Gd = 156.33$.

THORIUM.

Atomic weight redetermined by Urbain.[2] The thoria was purified by conversion into the acetyl acetonate, which was crystallized from solution in chloroform. It was then converted into sulphate. The atomic weight determinations (with $O = 16$), were made by calcination of anhydrous $Th(SO_4)_2$. Data as follows :

Weight sulphate.	Weight ThO₂.	Atomic weight Th.
1.0925	0.6815	233.30
0.5926	0.3699	233.75
1.0230	0.6384	233.58

Calcination of the hydrous sulphate gave lower values, probably because the octohydrated salt used contained traces of the sulphate with 9 molecules of water.

[1] *Ztschr. anorg. Chem.*, **22**, 393.
[2] *Ann. chim. phys.*, (7), **19**, 223.

MISCELLANEOUS NOTES.

Muthmann and Böhm[1] have prepared pure yttria by fractional precipitation with neutral potassium chromate. The final sample was practically pure, and gave a good atomic weight determination. 2.46585 grams sulphate yielded 1.19523 grams of oxide. Hence Yt = 88.97, when O = 16.

Samarium has been studied by Demarçay.[2] By synthesis of the sulphate he finds the atomic weight of the metal to range from 147.2 to 148.0, when O = 16. The higher values, about 150, obtained by other investigators, he attributes to the presence of other earths. In a second paper[3] he describes one of these earths, which is intermediate between samarium and gadolinium, with an atomic weight of the metal equal to 151, nearly. This, however, is only a rough approximation, as the oxide was not sufficiently pure for exact work.

The density of krypton has been carefully determined by Ladenburg and Krügel.[4] From it the atomic weight of the element becomes, in two experiments, 58.67 and 58.81, or 58.74 in the average.

Ramsay and Travers[5] give density determinations and atomic weights for the new gases of the atmosphere as follows:

	Density.	Atomic weight.
Helium ...	1.98	3.96
Neon ...	9.97	19.94
Argon ...	19.98	39.96
Krypton ...	40.88	81.76
Xenon ...	64.00	128.00

Metargon is abandoned, as non-existent. Why the value for krypton should diverge so widely from that found by Ladenburg and Krügel, is unexplained. It will be noticed that most of these gases fall between the halogens and the alkali metals in the periodic system, although argon is still slightly divergent from theory.

Mme. Curie has continued her studies upon radium,[6] which were referred to in the report for 1899. She now describes a

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1 *Ber. d. chem. Ges.*, **33**, 42.
2 *Compt. rend.*, **130**, 1185.
3 *Ibid.*, **130**, 1469.
   Chem. News, **81**, 205.
5 *Ibid.*, **82**, 257.
6 *Compt. rend.*, **131**, 382.

radiferous barium chloride in which the mixed metals have a mean atomic weight of 173.6 to 174. In this sample, judging from spectroscopic evidence, there was probably rather more radium than barium.

TABLE OF ATOMIC WEIGHTS.

The following table of atomic weights differs but little from that issued last year. First, your committee gives its own list, in two columns, representing both standards of value, H = 1, and O = 16. The only change here is in iron, due to the work of Richards and Baxter. Richards' table is unchanged, except in the same item. The table of the German Committee is that which was issued in January, 1901, as an insert to the first number of the *Berichte*.

	Clarke.		Richards.	German.
	H = 1.	O = 16.		
Aluminum	26.9	27.1	27.1	27.1
Antimony	119.5	120.4	120.0	120.
Argon	?	?	39.9?	39.9
Arsenic	74.45	75.0	75.0	75.
Barium	136.4	137.40	137.43	137.4
Bismuth	206.5	208.1	208.0	208.5
Boron	10.9	11.0	10.95	11.
Bromine	79.34	79.95	79.955	79.96
Cadmium	111.55	112.4	112.3	112.4
Caesium	131.9	132.9	132.9	133.
Calcium	39.8	40.1	40.1	40.
Carbon	11.9	12.0	12.001	12.00
Cerium	138.0	139.0	140.	140.
Chlorine	35.18	35.45	35.455	35.45
Chromium	51.7	52.1	52.14	52.1
Cobalt	68.55	59.00	59.00	59.
Columbium	93.0	93.7	94.	94.
Copper	63.1	63.6	63.60	63.6
Erbium	164.7	166.0	166.	166.
Fluorine	18.9	19.05	19.05	19.
Gadolinium	155.8	157.0	156.?	156.
Gallium	69.5	70.0	70.0	70.
Germanium	71.9	72.5	72.5	72.
Glucinum	9.0	9.1	9.1	9.1
Gold	195.7	197.2	197.3	197.2
Helium	?	?	4.0?	4.
Hydrogen	1.000	1.008	1.0075	1.01
Indium	113.1	114.0	114.	114.
Iodine	125.89	126.85	126.85	126.85
Iridium	191.7	193.1	193.0	193.
Iron	55.5	55.9	55.9	56.

	Clarke. H = 1.	Clarke. O = 16.	Richards.	German.
Krypton	....	....	....	81.8
Lanthanum	137.6	138.6	138.5	138.
Lead	205.36	206.92	206.92	206.9
Lithium	6.97	7.03	7.03	7.03
Magnesium	24.1	24.3	24.36	24.36
Manganese	54.6	55.0	55.02	55.
Mercury	198.50	200.0	200.0	200.3
Molybdenum	95.3	96.0	96.0	96.
Neodymium	142.5	143.6	143.6	143.6
Neon	...	....	....	20.
Nickel	58.25	58.70	58.70	58.7
Nitrogen	13.93	14.04	14.045	14.04
Osmium	189.6	191.0	190.8	191.
Oxygen	15.88	16.000	16.0000	16.00
Palladium	106.2	107.0	106.5	106.
Phosphorus	30.75	31.0	31.0	31.
Platinum	193.4	194.9	195.2	194.8
Potassium	38.82	39.11	39.140	39.15
Praseodymium	139.4	140.5	140.5	140.5
Rhodium	102.2	103.0	103.0	103.
Rubidium	84.75	85.4	85.44	85.4
Ruthenium	100.9	101.7	101.7	101.7
Samarium	149.2	150.3	150.0	150.
Scandium	43.8	44.1	44.	44.1
Selenium	78.6	79.2	79.2	79.1
Silicon	28.2	28.4	28.4	28.4
Silver	107.11	107.92	107.930	107.93
Sodium	22.88	23.05	23.050	23.05
Strontium	86.95	87.60	87.68	87.6
Sulphur	31.83	32.07	32.065	32.06
Tantalum	181.5	182.8	183.	183.
Tellurium	126.5	127.5?	127.5 ?	127.
Terbium	158.8	160.	160.	....
Thallium	202.61	204.15	204.15	204.1
Thorium	230.8	232.6	233.	232.5
Thulium	169.4	170.7	170.?	171.
Tin	118.1	119.0	119.0	118.5
Titanium	47.8	48.15	48.17	48.1
Tungsten	182.6	184.	184.4	184.
Uranium	237.8	239.6	240.	239.5
Vanadium	51.0	51.4	51.4	51.2
Xenon	....	....	....	128.
Ytterbium	171.9	173.2	173.	173.
Yttrium	88.3	89.0	89.0	89.
Zinc	64.9	65.4	65.40	65.4
Zirconium	89.7	90.4	90.5	90.7

THE DETERMINATION OF PHOSPHATES. IN POTABLE WATERS.

BY A. G. WOODMAN AND L. L. CAYVAN.

THE estimation of phosphates is a part of the sanitary examination of waters which has been somewhat neglected in the past, doubtless because the ordinary methods of determination are quite tedious and because the exact significance to be attributed to the presence and amount of phosphates is a question still in abeyance. There can be no question, however, in consideration of the probable decomposition and oxidation of the organic phosphorus compounds in animal excretions, that an excessive amount of phosphates in a water, unless otherwise accounted for, is an indication of pollution. If then the amount could be estimated by a method sufficiently simple and rapid, enough data might readily be gathered to render the determination of much greater value than at present. Especially would this be true in comparing several waters from the same locality.

Repeated trials of methods which have been proposed have shown that there is none which is perfectly satisfactory for accurate and rapid work. The extremely small quantities of phosphate found even in polluted waters would seem to preclude the use of gravimetric methods. Such methods, however, have been used. Hehner,[1] and also Harvey,[2] concentrate a large quantity of the water and determine the phosphate gravimetrically as ammonium phosphomolybdate. All gravimetric methods are objectionable on account of the time required. Furthermore, not being very delicate, they necessitate considerable concentration, which, as will be shown later, almost invariably occasions a loss of phosphate. Phipson[3] precipitates the phosphate from a large volume of water by means of alum and an excess of ammonia, making the final precipitation with ammonium molybdate. The process is a long one and experiments with a more delicate method showed that the precipitation of the phosphate is not complete.

[1] *Analyst*, 4, 23; and 5, 135.
[2] *Ibid.*, (1880), 197.
[3] *Chem. News*, 56, 251.

On the whole, the colorimetric methods seem best adapted for the determination. Several such methods have been proposed, based on the color given to dilute phosphate solutions by ammonium molybdate in the presence of nitric acid. Lepierre[1] evaporates a liter of water, dehydrates the silica by repeated evaporations with nitric acid, ignites strongly, and filters. The phosphate in the filtrate is estimated colorimetrically by ammonium molybdate. Jolles and Neurath[2] use potassium molybdate instead of the ammonium salt, and Jolles[3] has applied the method to the determination of phosphoric acid in water, removing the silica from the residue obtained by the evaporation of a liter of water by ignition at $130°$ C. These methods are open to the same objections as the gravimetric methods, namely that by requiring the evaporation of large quantities of water they introduce serious liability to error and are too tedious to be of general use. Furthermore, the temperature at which the residue should be ignited to remove silica is a matter of importance, especially when dealing with small amounts. In view of these considerations it was deemed advisable to make a critical study of the colorimetric methods.

APPARATUS AND REAGENTS.

Ammonium Molybdate.—50 grams of the pure neutral salt were dissolved in a liter of distilled water.

Nitric Acid (sp. gr. 1.07).—Approximately one part of acid (sp. gr. 1.42) to five parts of water.

Standard Phosphate Solution.—0.5324 gram of pure crystallized sodium phosphate ($Na_2HPO_4.12H_2O$) was dissolved in freshly distilled water, 100 cc. of nitric acid (1.07) added, and the whole diluted to 1 liter. This solution is diluted to make the standards. One cc. $=$ 0.0001 gram P_2O_5. The solution keeps without change for several months if preserved in well-stoppered bottles of hard glass; after a longer time it becomes slightly stronger, owing to the silica dissolved from the glass.

Standard Silica Solution.—About 5 grams of precipitated and washed silica were dissolved in an excess of sodium hydroxide made from metallic sodium. The solution was made faintly acid

[1] *Bull. Soc. Chim.*, 15, 1213 (1896).
[2] *Monatshefte*, 19, 5 (1898).
[3] *Archiv. f. Hygiene*, 34, 22 (1899).

with nitric acid, diluted to a definite volume, and the silica determined in an aliquot part. The standard solution was made by diluting this strong solution until 1 cc. = 0.001 gram SiO_2.

It was found that sodium or potassium molybdate offered no particular advantages over the ammonium salt. The color obtained was no more intense and was distinctly greener, which made the reading of the standards much more difficult. It was found also that for a given amount of the phosphate solution the depth of color and the rapidity with which it developed depended to a certain extent upon the quantity of reagents used. The best results were obtained by the use of 4 cc. of the ammonium molybdate solution and 2 cc. of the nitric acid.

For comparing the colors the ordinary Nessler tubes were used at first, but it was found that if tubes of too small diameter were used the colors were not easily read ; if of too large diameter the delicacy of the reaction is considerably decreased. The tubes which have been found most satisfactory have a capacity of 100 cc. They are of hard, white glass, about 2.5 cm. in diameter and 24 cm. long to the 100 cc. mark. The color is a rather difficult one to read closely and for very accurate readings probably some form of colorimeter could be used to advantage. For any but the most refined work, however, it will be found amply sufficient to compare the tubes by a north light against a reflecting white surface, such as a pure white unglazed porcelain tile supported at an angle of about 40°. This procedure was followed in all this work, and was found most practical where a number of tubes are to be compared rapidly.

Using no greater precautions than those just described, the delicacy of the test is considerable. If care is taken to choose two tubes, identical in all respects, it is possible to detect 0.002 cc. of the standard phosphate solution in 50 cc. of water. If the tubes are heated to 60° C. 0.001 cc. can be read. The delicacy of the reaction is therefore sufficient to show the presence of 1 part of phosphate as P_2O_5 in 500,000,000 parts of water. On the other hand, comparatively large quantities of phosphate may be present in 50 cc. of water, without causing precipitation or turbidity on the addition of the reagents except after standing a considerable time. On account of the difficulty in matching the more intense colors no higher standard than 10 cc. of the standard

solution in 50 cc. of water is ever used, and it has been determined by direct experiment that a standard as high as this will not become turbid at room temperature for twelve or fifteen hours. The color of the phosphate standard is an additive property ; it makes no difference, apparently, whether the higher standards are made up directly or by the addition of more of the standard solution to the lower standards.

The question of the permanency of the phosphate standards was one of the first ones investigated. Lepierre, in the article previously cited, stated that the phosphate standards can be preserved for several months without change. Careful comparison of a number of standards from day to day, however, showed that this was not strictly true. The change in some of the higher standards while slight was still distinctly noticeable when carefully observed, and in others, especially the lower ones, the color faded so much in two or three days that the standards were rendered useless. Nor was any other substance found giving the right color which was suitable for the preparation of permanent standards. The most satisfactory was a dilute solution of picric acid, which gave a yellowish green color very similar to the phosphate color. But it was found impossible to keep even these standards in glass tubes since the solvent action on the alkali of the glass was sufficient to form a slight amount of the alkali picrate, which has a more intense color than the picric acid itself; hence, the standards slowly increased in color. The attempt was therefore abandoned and fresh phosphate standards were used for all comparisons.

STUDY OF THE PHOSPHATE REACTION.

For a given volume of water and a definite amount of reagents the depth of the phosphate color is a function of two factors ; namely, the amount of phosphate present and the temperature. To determine the exact effect of the latter for the conditions employed in this work, readings of various phosphate standards were made at different temperatures. Differing amounts of the standard solution were diluted to 50 cc., and, after the addition of the reagents, were heated gradually in a water-bath from 20° to 60° C. Readings were taken every 5°. If the reagents are added after heating, the colors are not so clear. The heating was

not carried beyond 60° because above this temperature the standards become cloudy and the higher standards tend to precipitate. The maximum color is given between 90° and 100°, but the tendency to precipitation renders the reading at this temperature impracticable. The most satisfactory colors are obtained at 20°– practically at room temperature. A variation of a few degrees causes only a slight error. The results are given in the following table :

Amounts phosphate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
6 cc.........	6.2	7.2	7.7	8.2	8.7	9.6	...	10.2
	6.2	7.2	7.8	8.3	8.7	10.2	10.4	10.7
	6.2	7.7	8.2	9.0	9.2	9.7	10.4	10.3
Average	6.2	7.3	7.6	8.5	9.0	9.8	10.4	10.5
5 cc.........	5.1	5.9	6.6	7.3	7.8	8.0	8.6	9.6
	5.1	5.3	6.1	7.2	7.9	8.4	8.6	9.4
	5.1	5.2	6.3	7.1	8.0	8.3	8.7	8.9
	5.1	5.6	6.6	7.0	7.8	8.5	8.6	9.2
Average	5.1	5.5	6.4	7.2	7.9	8.3	8.6	9.2
4 cc.........	4.1	4.7	5.1	5.4	6.4	6.6	6.9	7.1
	4.1	4.8	5.1	5.5	6.4	6.5	6.8	7.3
	4.1	4.8	5.1	5.5	6.4	6.6	7.0	7.4
Average	4.1	4.7	5.1	5.5	6.4	6.6	6.9	7.2
3 cc.........	3.1	3.4	3.9	4.5	5.1	5.7	5.8	6.2
	3.4	3.7	4.4	4.7	5.2	5.3	5.7	5.9
	3.2	3.7	3.9	4.3	4.9	5.4	5.5	6.2
Average	3.2	3.6	4.1	4.5	5.1	5.5	5.7	6.1
2 cc.........	2.2	2.5	2.7	2.9	3.1	3.4	3:6	3.9
	2.2	2.5	2.8	3.1	3.2	3.4	3.7	3.9
	2.4	2.6	2.9	3.0	3.3	3.4	3.5	3.9
Average	2.2	2.5	2.8	3.0	3.2	3.4	3.6	3.9
1 cc.........	1.1	1.2	1.4	1.5	1.5	1.7	1.9	1.9
	1.1	1.2	1.3	1.4	1.5	1.7	1.8	1.8
	1.1	1.2	1.4	1.5	1.5	1.5	1.7	2.0
Average	1.1	1.2	1.4	1.4	1.5	1.6	1.8	1.9
0.7 cc......	0.75	0.80	0.85	0.95	1.1	1.2	1.25	1.27
	0.75	0.80	0.85	0.90	1.05	1.15	1.25	1.28
	0.75	0.80	0.83	0.95	1.05	1.15	1.20	1.25
Average	0.75	0.80	·0.85	0.93	1.05	1.17	1.22	1.26

Amounts phosphate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
0.5 cc......	0.60	0.65	0.70	0.80	0.90	0.95	1.05	1.10
	0.60	0.60	0.65	0.75	0.85	0.90	0.95	0.95
	0.60	0.65	0.70	0.75	0.85	0.85	0.95	0.95
Average	0.60	0.65	0.70	0.77	0.87	0.90	0.98	1.01
0.4 cc......	0.45	0.50	0.55	0.65	0.70	0.75	0.80	0.80
	0.45	0.55	0.55	0.57	0.60	0.65	0.70	0.70
	0.45	0.55	0.55	0.58	0.65	0.67	0.70	0.70
Average	0.45	0.53	0.55	0.60	0.65	0.68	0.72	0.72
0.3 cc......	0.33	0.36	0.39	0.44	0.48	0.58	0.63	0.68
	0.33	0.36	0.39	0.45	0.50	0.55	0.60	0.65
	0.33	0.36	0.39	0.44	0.54	0.58	0.60	0.65
Average	0.33	0.36	0.39	0.44	0.51	0.57	0.61	0.66
0.2 cc......	0.23	0.27	0.31	0.32	0.34	0.37	0.38	0.39
	0.23	0.27	0.30	0.33	0.33	0.36	0.38	0.39
	0.23	0.27	0.30	0.33	0.34	0.37	0.38	0.39
Average	0.23	0.27	0.30	0.33	0.34	0.37	0.38	0.39
0.1 cc......	0.11	0.13	0.14	0.16	0.17	0.18	0.19	0.20
	0.12	0.13	0.14	0.16	0.17	0.18	0.19	0.20
Average	0.11	0.13	0.14	0.16	0.17	0.18	0.19	0.20

Some of the results are shown graphically in Fig. 1, in which readings have been taken as ordinates and temperatures as abscissas. The curves show slight irregularities, due to the difficulty of reading exactly. The increase in color with increased temperature is considerable, double in the higher standards. All of the standards on cooling go back to less than their original color. No case of precipitation occurred, although some of the highest standards were too turbid to be read easily.

Several of the methods previously proposed for the determination of phosphates involve the concentration of the water, followed by heating at various temperatures. Preliminary experiments had shown the liability to loss during such procedure, and the point was further investigated. One liter of water, containing 5 cc. of phosphate solution and 2 cc. of nitric acid, was evaporated to dryness; a loss of 16 per cent. of the phosphate occurred. Phosphate standards made up in a volume of 50 cc., with varying amounts of nitric acid, were evaporated to dryness and some of them heated in an air-bath at 100° for periods varying from
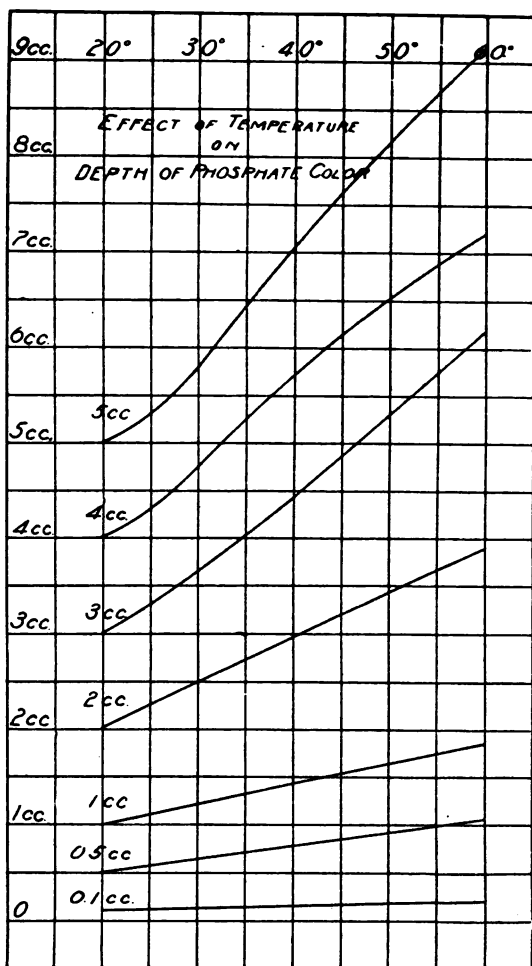
Fig. 1.

fifteen minutes to two hours. A loss of phosphate always occurred whether done in platinum or porcelain dishes. Other standards were evaporated and heated at 135° C., still others were ignited over a free flame ; a loss was found in all cases. An idea of the magnitude of the loss may be gained from the following figures :

EVAPORATED WITHOUT NITRIC ACID AND HEATED ONE HOUR AT 100°.

	In porcelain dishes.						In platinum dishes.					
Amount added	0.1	0.2	0.5	1.0	2.0	5.0	0.1	0.2	0.5	1.0	2.0	5.0
" found	0.1	0.18	0.45	0.75	1.8	4.9	0.07	0.12	0.4	0.85	1.8	4.9

EVAPORATED AS ABOVE BUT HEATED ONE HOUR AT 135°.

	In porcelain dishes.						In platinum dishes.					
Amount added	0.1	0.2	0.5	1.0	2.0	5.0	0.1	0.2	0.5	1.0	2.0	5.0
" found	0.0	0.0	0.0	1.0	1.5	4.0	0.0	0.0	0.1	0.6	1.3	2.7

In all cases where nitric acid was used and the residue was heated at 100°, the loss on a 2 cc. standard was from 0.02 to 0.22 cc. greater the more acid used. Where the ignition was made over a free flame the loss varied from 25 to 50 per cent., highest in the low standards. Without the addition of nitric acid the loss on evaporation was very irregular. In the presence of a definite quantity of acid the loss was more nearly constant. Without going into great detail it may be said that it was apparent that the loss was due to some change taking place while the solution is dilute and hot. The total loss occurs usually during the concentration of the solution to one-half its volume.

THE EFFECT OF SILICA.

The properties of dilute solutions of ammonium silicomolybdate were also studied since silica is the principal substance which interferes with the phosphate test.

Solutions made up with varying quantities of the standard silica solution gave a color immediately upon adding the reagents. With small and medium amounts of silica the color was slight compared with that developed in an hour ; with high silica standards considerable color developed instantly. It is interesting to note that ammonium molybdate alone with a silica solution made exactly neutral, develops a faint color in an hour, but with a phosphate standard no color appears except in the presence of nitric acid. In twenty-four hours the color due to the silicomolybdate fades appreciably ; it is greener than the color of the phosphomolybdate.

To determine the time necessary for silica standards to attain their maximum color varying standards were mixed with the reagents and 50 cc. of water and compared at definite intervals

with fresh phosphate standards. The readings in terms of the standard phosphate solution are given in the following table :

cc. SiO$_2$ used.	1/2 hour.	1 hour.	1.5 hours.	2.5 hours.	3 hours.	3.5 hours.
0.1	0.03	0.07	0.09	0.03	0.02	0.03
0.7	0.56	0.65	0.67	0.72	0.70	0.67
1.0	0.92	0.96	1.01	1.02	1.07	1.05
3.0	2.75	2.88	2.95	3.01	2.95	2.95
7.0	6.65	6.75	6.95	7.00	7.10	7.20
10.0	9.70	9.95	9.99	9.95	9.95	...

cc. SiO$_2$ used.	4.5 hours.	5 hours.	5.5 hours.	6 hours.	6.5 hours.	7 hours.
0.1	0.02	0.01	0.01	0.01	0.008	0.008
0.7	0.67	0.67	0.66	0.66	0.65	0.65
1.0	1.05	1.04	1.03	1.03	1.02	1.02
3.0	3.10	3.20	3.20	3.25	3.30	3.40
7.0	7.20	7.20	7.25	7.25	7.30	7.35
10.0	9.95	9.95	9.95	9.95	9.95	9.90

It will be noticed that the lower standards reach a maximum in about two or three hours, and then begin to fade ; the medium standards do not seem to reach a maximum even after seven hours.

A number of silica standards, after standing one hour, were heated from 20° to 100° in a water-bath. The color did not change in intensity until 70°–80° was reached, when it began to fade, decreasing up to 100°. The color did not return to its original intensity on cooling slowly to 20°.

Experiments made to determine the conditions under which minute quantities of silica might be rendered entirely insoluble, showed that evaporation with nitric acid and heating at 100° for an hour was insufficient ; when the same standards were evaporated and heated at 135° for an hour, recombination took place and some of the silica remained soluble. On heating the residues for *two* hours at 100° instead of one hour, however, no silica remained soluble. The results are shown in the following table : 1, 2, and 5 cc. of the standard silica solution were diluted to 50 cc., 10 drops of nitric acid were added, the solutions evaporated to dryness in porcelain dishes, and heated at different temperatures for two hours. The residue was taken up in cold water and the color read after standing one hour :

Temperature.	Readings.			Per cent. undehydrated SiO_2.		
	1 cc.	2 cc.	5 cc.	1 cc.	2 cc.	5 cc.
60°	0.5	1.2	2.0	50	60	40
80°	0.3	0.7	0.9	30	35	18
100°	0.0	0.0	0.0	00	00	00
135°	0.1	0.4	1.0	10	20	20
150°	0.4	0.5	1.1	40	25	22
190°	0.6	0.8	1.1	60	40	22

These results are shown graphically, using percentages of undehydrated silica as ordinates and temperatures as abscissas, in Fig. 2.
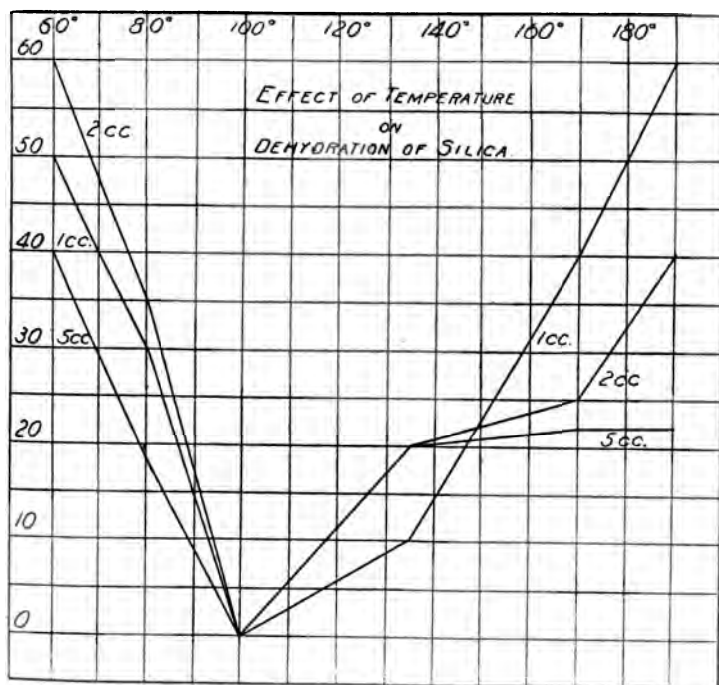
Fig. 2.

OTHER COMPOUNDS WHICH MIGHT INTERFERE.

Since vanadium and titanium resemble phosphorus and silicon quite closely in many of their properties, vanadates and titanates might interfere with the determination of phosphates by a colori-metric method. Titanium is especially liable to occur in the

natural waters of regions containing diorites and titanium-bearing ores like ilmenite. The presence of these elements has been observed in natural waters.

Dilute solutions of sodium titanate gave a pale greenish yellow color with ammonium molybdate and nitric acid, but much less intense than the phosphate color. The color did not fade within an hour, but at 20° C. it took twelve minutes for it to appear. By evaporation with nitric acid, and subsequent heating at 100° for two hours, the titanium oxide was rendered completely insoluble.

Ammonium vanadate gave with the ammonium molybdate *alone* a yellow color which was permanent for several hours, but upon the addition of nitric acid this color faded completely in five minutes. Experiments with a standard solution of ammonium vanadate showed that the color given by as much as 0.0003 gram of V_2O_3 in 50 cc. of water fades out entirely in four minutes. Incidentally it was found that 0.000001 gram of V_2O_3 could be detected readily in a volume of 50 cc. It is evident that the small quantities of vanadium which occur in natural waters will not interfere with the determination of phosphates.

COLORIMETRIC ESTIMATION OF PHOSPHATES IN THE PRESENCE OF SILICA.

The previous results had shown the possibility of a method based on the dehydration and elimination of the silica. The conditions must be such that the total phosphate or a definite portion of it shall be left intact and that the silica shall be rendered entirely insoluble. The following method was finally adopted as the one giving the most satisfactory results :

Fifty cc. of the water and 3 cc. of nitric acid (sp. gr. 1.07), are evaporated to dryness in a 3-inch porcelain dish on a water-bath. The residue is heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with 50 cc. of cold distilled water, added in several portions, and poured into the comparison tube. It is not necessary to filter the solution. Four cc. of ammonium molybdate and 2 cc. of nitric acid are added, the contents of the tube mixed, and the color compared after three minutes with standards made by diluting varying quantities of the standard phosphate solution to 50 cc., and

adding the reagents as above. A blank should always be made on the distilled water used for dilution, especially if it has stood for any length of time in glass vessels.

The method as just described will be sufficient for ordinary work. If a more exact determination of the phosphate is required a slight correction should be applied in each case. These corrections were determined by making a number of determinations by the method. The results are shown in the following table. The first two series had 2 cc. of standard silica solution added to each test ; the others had only the phosphate.

Phosphate added.	Phosphate found.						Average.	Correction.
0.1	0.07	0.09	0.10	0.10	0.09	0.09	0.09	0.01
0.5	0.46	0.47	0.46	0.45	0.43	0.45	0.45	0.05
0.7	0.63	0.64	0.64	0.65	0.64	0.66	0.65	0.05
1.0	0.85	0.85	0.86	0.86	0.84	0.83	0.85	0.15
3.0	2.55	2.65	2.50	2.50	2.60	3.65	2.60	0.40
5.0	4.55	4.55	4.45	4.45	4.50	4.50	4.50	0.50
7.0	6.65	6.60	6.55	6.55	6.60	6.65	6.60	0.40
10.0	9.60	9.65	9.55	9.60	9.60	9.55	9.60	0.40

Since organic life is present in greater numbers and is more active in surface waters than in ground waters, it is evident that the determination will be of greatest value for the examination of wells. Well waters are usually colorless, and to them the method may be applied directly. It is not yet suitable for colored waters. The determination of phosphates is at present being carried on in this laboratory as a routine determination and the results will be published as soon as sufficient data have accumulated to render a discussion of the entire question of value.

BOSTON, MASS., December 20, 1900.

EXPERIMENTS ON CHALCOPYRITE.

BY LEONARD P. MORGAN AND EDGAR F. SMITH.

AT various times experiments have been made in this laboratory looking to the determination of the constitution of certain natural chemical products. Thus, the state of oxidation of the iron in pyrite, marcasite, and arsenopyrite has received

considerable attention, and in the present communication it is
desired to give the results of similar experiments made upon the
mineral chalcopyrite. Weighed portions of the latter were
exposed in porcelain boats to the action of dry hydrochloric acid
gas. As the mode of procedure has been sufficiently detailed in
former papers, it may be omitted here. It will suffice to note
that the heat was obtained from a single Bunsen burner with a
wing top. The period of heating covered one hour, beginning
of course with a gentle heat and increasing finally to a full red
heat. The boat and contents were allowed to cool in the gas.
On their withdrawal from the tube they were placed in a beaker
containing distilled water. The combustion tube was also
washed out carefully with water. The aqueous solution of the
iron salt was strongly diluted, acidified with sulphuric acid and
the liquid titrated with potassium permanganate.

RESULTS.

	Chalcopyrite. Gram.	Iron found. Gram.	Iron found. Per cent.
1	0.2112	0.06489	30.72
2	0.2039	0.06231	30.56
3	0.2007	0.06164	30.70
4	0.1996	0.06128	30.67
5	0.2089	0.06398	30.63
6	0.2140	0.06553	30.62

In several instances the liquid in the receiver placed at one end
of the combustion tube showed traces of ferric iron when the
thiocyanate test was applied. This might readily occur when
it is remembered that the quantity of ferrous chloride thus vol-
atilized was exceedingly small and that its exposure during the
time required for the completion of the experiment would be
enough to cause its oxidation. However, the quantity of ferric
iron was extremely small.

The formula generally assigned the mineral is $CuFeS_2$, which
would require 30.5 per cent. of iron. The results given above
therefore indicate a complete decomposition of the material by
hydrochloric acid, and also show that all of the iron is in the fer-
rous state. This proved to be the case with marcasite. As
hydrochloric acid gas does sometimes act as a reducing agent,
there was a possibility that perhaps it might have transformed
any ferric iron present in the mineral into the ferrous condition.

To render the results as certain as possible, portions of the mineral were carefully heated in sealed tubes with a solution of copper sulphate, as had been done with marcasite. The evidence gathered in this way corroborated the first experience and it can safely be asserted that chalcopyrite contains all of its iron in the ferrous form, and that the mineral is, perhaps, nothing more than a substituted marcasite, in which copper has replaced its equivalent of iron.

UNIVERSITY OF PENNSYLVANIA.

ON TRIPHENYLCHLORMETHANE.

BY M. GOMBERG.

THE recent publication by Norris and Sanders[1] on the same subject induces me to make a few remarks at this time. It is far from my intention to enter into any controversy whatever. I merely wish to call attention to the following few points :

(1) My paper on "Triphenylchlormethane"[2] was first presented by me at the Columbus Meeting of the American Association for the Advancement of Science, August, 1899. Norris and Sanders state that they have been at work on this subject for about a year. Hence this subject must have been undertaken by them after my paper was presented. It was, however, entirely natural that they should have overlooked the first mention of my paper, since it was given in the Proceedings[3] only by title.

(2) The difference in procedure between my method and that of Norris and Sanders consists in that the latter used, instead of benzene as a solvent, carbon disulphide,—a diluent first introduced by Anschütz[4] for Friedel and Crafts' reaction in general. The application of this solvent in the present instance enabled Norris and Sanders to isolate the important intermediate product, the double salt of aluminum chloride and triphenylchlormethane, which was not obtained by me at all.

(3) Norris and Sanders state[5] that the action of sodium upon triphenylchlormethane is entirely negative, even on two weeks'

[1] Am. Chem. J., 25, 54.
[2] This Journal, 22, 752.
[3] Proceedings American Association for the Advancement of Science, 48, 152 (1899).
[4] Ann. Chem. (Liebig), 235, 341.
[5] Loc. cit., p. 59.

contact in etner.   Only on the addition of brombenzene to the
above mixture did a reaction take place.   One of the several
products was a body free from halogen, yet on analysis the car-
bon and hydrogen did not add up to 100 per cent.   The fact that
'' this compound resembles closely in melting-point, chemical com-
position, and solubility'' the substance (the peroxide) described
by me[1] shows that it is an oxygen body.   One fails to see, however,
how Norris and Sanders '' discovered that an oxygen compound
was formed as the result of the action of sodium on a mixture of
triphenylchlormethane and   brombenzene.''   No evidence   is
given that they excluded all oxygen-carrying reagents, such as
sodium oxide, and that this was not the cause of the formation
of that body, or that they worked in an atmosphere free from
oxygen, and in this way established the non-formation of that
body under these conditions.   Furthermore, if the substance is
really identical with the peroxide mentioned, it is not the result
of the action of sodium upon a mixture of the two halogen com-
pounds, but is formed by action of the atmospheric oxygen upon
the unsaturated hydrocarbon (triphenylmethyl) which must have
resulted in some way from the action of sodium upon triphenyl-
chlormethane alone.[2]   The reaction must, therefore, be analogous
to that described by me for other metals : silver, zinc, and mer-
cury.   Only these three metals, in addition to the unsatisfactory
results with sodium, are mentioned in my preliminary paper.
Other metals, however, and different solvents, have also been
tried and are being studied at present.   Norris and Sanders now
'' propose to investigate the action of sodium on ethereal solutions
of triphenylchlormethane of varying concentrations.''   I regret
that having cleared up the difficult part of the problem (the
action of metals upon triphenylhalogenmethanes) I am not to
have, as it appears from Norris' publication, this field to myself
for a while longer.   It was stated[3] in my preliminary paper that
only about two-thirds of the theoretical quantity of the unsatura-
ted hydrocarbon is formed.   The nature of the other products is
being studied and I find that this varies according to the metal
and solvent employed.

UNIVERSITY OF MICHIGAN, CHEMICAL LABORATORY,
                    January 9, 1901.

[1] This Journal, 22, 762.

[2] Experiments show that small quantities of the triphenylmethyl are produced in this
way.

[3] This Journal, 22, 766.

SOLUBLE ARSENIOUS OXIDE IN PARIS GREEN.

PRELIMINARY REPORT.

By S. Avery and H. T. Beans.

FOR the past six months, the authors of this article have been engaged in .a more or less complete investigation of the arsenical insecticides, and while working with Paris green devoted considerable time to the study of the so-called "soluble or free arsenious oxide," and methods for its determination.

The recent appearance of two articles in this Journal, giving results somewhat different from those obtained by us, has induced us to present some phases of our work in this preliminary report.

Briefly, so much of these articles as has to do with the subject under consideration may be summed up as follows :

In his work on Paris green, J. K. Haywood[1] tried three methods for the determination of soluble arsenic.

1. A quantity of Paris green was weighed on a filter and extracted with cold water. Arsenic trioxide was found in the filtrate after 2 liters of water had been used and the method was abandoned.

2. Portions of 1 gram each were suspended in 500 cc. of water in stoppered flasks and the arsenic trioxide in solution determined every few days. The following table of results is given :

		Time in days.	Arsenic trioxide extracted. Per cent.
Paris green A		2	1.01
" "		4	1.68
" "		8	2.69
" "		11	4.02
" "		14	4.02
" "	B	9	3.41
" "		12	4.86
" "		14	4.86

The author says, "It will be seen that this method finally gave constant and very likely correct results."

3. Extraction with water kept at 50° to 60°. The solution was filtered off and replaced by fresh water each day.

[1] This Journal, 22, 768.

Time in days.	Total arsenic trioxide extracted. Per cent.
1	3.41
2	5.55
3	7.11
4	8.28
5	9.54
6	11.10
7	Still gaining

Since publishing the above, Haywood[1] has observed that in applying the second method above, some copper is obtained in the filtrate, indicating either the solubility of Paris green in cold water or its decomposition by that medium. He favors the former view, and to increase the accuracy of the method, determines the copper in solution and deducts the corresponding amount of arsenic trioxide from the total arsenic trioxide in the solution.

"It is of course possible, even probable," he says, "that the arsenious and copper oxides of Paris green do not go into solution in water in the same proportion that they are present in the original compound, but in the present state of our knowledge it seems to be the most plausible assumption that they do."

The second article mentioned is one by E. W. Hilgard.[2] The author states that a correction based upon the amount of copper in solution cannot be made since the copper and arsenic do not dissolve in the same proportion in which they are present in the original substance. As an illustration he gives an experiment in which cold water was allowed to slowly percolate through a sample of Paris green. After the passage of 2 liters there was no reaction for copper, though the arsenic continued to be extracted even after the fifth liter. No crystals of arsenic trioxide could be detected by the microscope in the residue thus washed, but only fragments of crushed globules.

In our work on the subject we used a large number of samples. Several samples of Paris green were made in the laboratory as well as other members of the series containing formic, propionic, and butyric acids, respectively, instead of acetic acid. We studied these as well as many commercial samples of Paris green. We shall confine this report, however, to experiments with one sample which we believe to be nearly pure for the reasons: (1) The

[1] This Journal, 22, 705.
[2] Ibid., 22, 690.

analysis showed the percentages of cupric oxide and of arsenic trioxide to be nearly in the proportions required by Ehrmann's formula. (2) By treatment with boiling sodium acetate solution according to the method given later in this paper, less than 1 per cent. of arsenic was extracted. (3) The most careful microscopic examination failed to disclose anything but bright spheres of Paris green. (4) The unground sample on standing with water gave off soluble arsenic at a slower rate than any other sample that we have examined.

The sample was divided into two portions : Sample "A" was left in the original condition. In Sample "B" the granules of
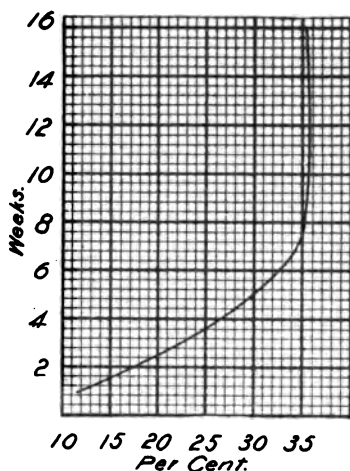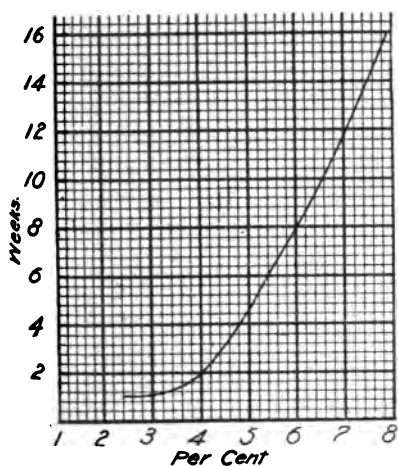
Paris green were broken by grinding in a mortar. Several lots of 0.5 gram were weighed from each of these samples and suspended in 500 cc. of distilled water contained in tightly stoppered cylinders. At the end of every two weeks, 250 cc. of the solution were filtered off and titrated with standard iodine. The results of this experiment are plotted in two curves here given, in which the time in weeks is given as ordinates and the percentage of. arsenious oxide in solution as abscissas. Owing to the marked difference in the rate of solution, the two curves are not drawn to the same scale.

In Curve "B" there is a gradual increase in soluble arsenic trioxide up to about the end of eight weeks when 35 per

cent. is reached.   Beyond this time the increase is slight, being only 0.14 per cent. from the twelfth to the sixteenth week.   At this time there was found in the filtrate 5.98 per cent. cupric oxide probably as copper acetate.

Had the copper and arsenious oxides gone into solution in the proportion in which they were present in the original sample, there should have been 19.57 per cent. cupric oxide instead of 5.98 per cent. in solution.   It might be urged that the excess of arsenic over copper might be due to uncombined arsenic trioxide in the sample.   Such an assumption would require at least 25 per cent. of uncombined arsenic trioxide.

While our results are in harmony with Hilgard's conclusion that copper and arsenic do not dissolve in the proportions in which they exist in Paris green, no close comparison of the experiments can be made as the experiments were made under different conditions.   In our work all the products remained in the sphere of action.   In Hilgard's work all soluble products were allowed to filter out as fast as formed.   His green seems, also, to have been exposed to the action of the air during the percolation.

We believe that the action of water on Paris green is a hydrolytic action.   Leaving out of consideration the probable formation of secondary products, it is probable that a small amount of copper acetate (whence the soluble cupric oxide), soluble arsenic trioxide, and basic copper acetate are formed. The reaction seems to take place in accordance with the law of mass action, a state of equilibrium being reached when about 36 per cent. of arsenic trioxide has passed into solution under the conditions previously stated.   It is quite likely that all the arsenic could be rendered soluble by replacing the supernatant liquid with fresh water from time to time and allowing to stand for a longer period.   In addition to the evidence already cited in support of this view it may also be added that the analysis of one residue showed 42.92 per cent. cupric oxide.   The analysis of another showed 50.61 per cent. cupric oxide.   This would be in harmony with the assumption of an increasing amount of basic acetate in the residues as the arsenic goes into solution.

We do not wish to lay any great stress on the probable nature of the products of the hydrolysis.   We do, however, assert that

all samples of Paris green that we have examined (some of them nearly pure so far as can be determined by all known tests) are decomposed into soluble arsenic ; that we have extracted 36.79 per cent. (considerably over one-half) of arsenious oxide from a sample which we have every reason to believe was practically pure, and that in all cases examined the per cent. of copper in the residue increases as the arsenic passes into solution.

It is, of course, reasonable to suppose that the same kind of action takes place with the unground sample, only much more slowly. The Curve "A" shows plainly that the condition of equilibrium has not yet been reached and probably the arsenious oxide would go into solution till the maximum quantity of about 36 per cent. had been reached.

From these experiments it would seem that, while a fair approximation to correct results may be obtained in some cases by suspending Paris green in 1000 parts of water and allowing to stand for a week, the method is quite arbitrary. In none of our work have we noticed any marked change in the rate of solubility at any particular time. On the contrary, the amount of arsenic trioxide in solution appears to depend almost entirely on the length of time of action, the concentration of the solution, and the state of division of the particles of Paris green. To obviate the above difficulties as far as possible, we have used a strong solution of sodium acetate instead of water. The use of such a solution has two advantages. In the first place, arsenic trioxide is much more readily soluble in a solution of sodium acetate than in water, hence much less time is required and consequently there is much less liability to decompose the Paris green.

Of much more importance, however, is the fact that the presence of sodium acetate in the solution largely prevents the hydrolyzing action of water on the compound, thus giving a somewhat sharper distinction between free arsenic trioxide and arsenic trioxide rendered free by hydrolytic action. While we believe this method better than the one in common use, it still leaves much to be desired.

For the determination we digest over the open flame 1 gram of the Paris green for about five minutes with 25 cc. of a solution of sodium acetate containing 12.5 grams of the crystallized salt.

The solution is then cooled, made up to 100 cc. and 50 cc. filtered off and titrated with standard iodine in the usual way.

In connection with this series of experiments, we tried the action of carbon dioxide on Paris green suspended in water. One gram of Paris green from the same sample as was used in the previous experiments and in its original condition, *i. e.*, not pulverized, was suspended in 500 cc. of water for one week, the water being kept saturated with pure carbon dioxide. At the end of this time the arsenic trioxide in solution amounted to 27 per cent. of the weight of the Paris green taken, or 48.5 per cent. of the total arsenic trioxide present had dissolved. There was also a little copper in solution, but this was not determined. The color of the residue changed from a bright green to a dull earthy color, some particles becoming nearly black. Had the sample been pulverized, the decomposition would probably have been practically complete.

As the result of our work, it seems to us that too much importance is being attached to the content of "soluble arsenious oxide" in Paris green. In the first place, since Paris green is of no very definite composition, and since water so easily hydrolyzes it into its constituents, the analytical results for "soluble arsenic" are uncertain and quite dependent on the conditions of the determination. In the usual method of analysis there is no method of distinguishing between the amount of "free arsenic trioxide" and "arsenic trioxide rendered free by hydrolysis." The extent of the hydrolysis is determined mainly by the length of time the water is in contact with the Paris green, and the state of division of the particles. This latter factor exerts by far the greater influence and is wholly beyond the control of the analyst. While the size of the spherical granules is fairly constant in any one sample, different samples show the widest variation. Aside from this variation in the particles themselves, nearly all samples contain a considerable proportion of broken granules of varying degrees of fineness.

Hilgard and others give 4 per cent. as the maximum amount of soluble arsenic trioxide a Paris green should contain if it is to be used for spraying purposes. The purest sample we have obtained gave 2.61 per cent. after standing in water for one week and 4 per cent. at the end of two weeks. A portion from the

sample after being ground was treated in the same way, giving 10.55 per cent. in one week and 17.51 per cent. at the end of two weeks, thus showing both the limitations of the present method of analysis and the marked influence of the state of division on the results.

In view of the fact that carbon dioxide, in the presence of water, so readily decomposes Paris green converting at least one-half of the arsenic trioxide into the soluble condition, it would seem that even if an absolutely pure sample were used in spraying, it might easily happen that the carbon dioxide and water-vapor of the air would convert much more than the limiting 4 per cent. arsenic trioxide into the free state. Probably many of the irregularities observed in the action of Paris green on foliage could be directly traced to weather conditions which happen to be favorable to the formation of free arsenic trioxide from a comparatively pure sample of Paris green.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF IDAHO.

NEW BOOKS.

GRUNDZÜGE DER SIDEROLOGIE. VON HANNS FREIHERR V. JÜPTNER. ERSTER TEIL ; DIE KONSTITUTION DER EISENLEGIERUNGEN UND SCHLACKEN. Leipzig: Verlag von Arthur Felix. 1900. Price, 13 M.

The author of this interesting and valuable work contends that the science of iron, while still far from mature, as we all know, has now become old enough to have a name of its own, and he proposes to call it "Siderology." This name is to be applied to that science which concerns itself not only with the intimate morphological and chemical constitution of iron alloys, but also seeks to determine in what ways these alloys or compounds are affected by outward influences, such as mechanical and heat treatment, and what connection exists between them and the physical and mechanical properties of iron and steel. In the author's view, metallography (Osmond) or siderography (Jüptner) bears the same relation to the science of siderology as petrography bears to the science of geology.

The work is to appear in three parts, of which the present volume of 315 pages is Part First. It covers theory of solution, micrography, the chemical constitution of iron alloys, and the chemical constitution of slags. The second part will treat of the

relation between chemical constitution, mechanical treatment, microscopic structure, and other properties of iron and steel. The third part will treat of the reactions between metal, slags, and other agents. The first 62 pages on "Theory of Solution" constitute a valuable scientific introduction to the study of iron alloys. In the chapter on micrography the methods of preparing and examining iron and steel under the microscope are given, with illustrations. Nearly all the more important work on those microscopic constituents of iron and steel which have been isolated, or otherwise identified, is here brought together in compact and convenient form. The author falls into an error, however, when he states that titanium appears to occur as such dissolved in iron. In pig-iron it is known to occur, and has been separated from it, combined with carbon as TiC in microscopic, cubical crystals.

The work closes with many valuable and probably fairly complete references to larger works and scattered papers on theory of solution, micrography, chemical constitution of iron alloys, and constitution of slags.   P. W. SHIMER.

LEHRBUCH DER ANORGANISCHEN CHEMIE. VON PROF. DR. H. ERDMAN. Zweite Auflage, mit 287 Abbildungen, einer rechen Tafel und sechs farbigen Tafeln. Braunschweig : F. Vieweg & Sohn. 8vo. xxvi + 758 pp. Price, 16 M.

A great many topics have been well handled and some of them quite fully treated. The tables of spectra of the "Edelgase," xenon, krypton, argon, neon, and helium, are beautiful pieces of work. The description of the separation of these gases and the liquefaction of air and kindred topics occupy considerable space ; the author enlarges on electrolytic dissociation, the ions, osmotic pressure, and kindred topics.

Less fortunate is the treatment of subjects belonging to chemical technology, which are, in a few cases, very badly handled.

No references are given to original memoirs. The synonyms are very fully given. In many cases the Russian name is printed and its pronunciation (in italic type) as well. The illustrations and the mechanical execution are up to the high standard so long maintained by this famous publishing house.   E. H.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

STUDIES ON SOLUTIONS OF STANNOUS SALTS.

II. THE OXIDATION OF SOLUTIONS OF STANNOUS CHLORIDE BY MEANS OF FREE OXYGEN.

By S. W. Young.

Received December 14, 1900.

PART. I.   THE RATE OF OXIDATION.

THE following paper gives some of the results thus far obtained from a study of the rate of oxidation of stannous chloride solutions by means of free oxygen. Although the investigation is only in the beginning stage it seems that, on account of the rather unusual results obtained, and on account of the fact that this particular work is, for a few months, necessarily interrupted, it may be well to publish the results already at hand.

The method used consisted in thoroughly shaking a solution of stannous chloride in an atmosphere of pure oxygen and measuring the decrease in volume, for definite periods of time, by means of a gas-burette. Thus far all measurements have been made at atmospheric pressure. The shaking apparatus is described here somewhat fully as it is thought that it may possibly be of service to others. It consists of a flask (Fig. 1) with two outlets, *a* and *b*. When the apparatus is in use, *a* is used for filling and *b* is
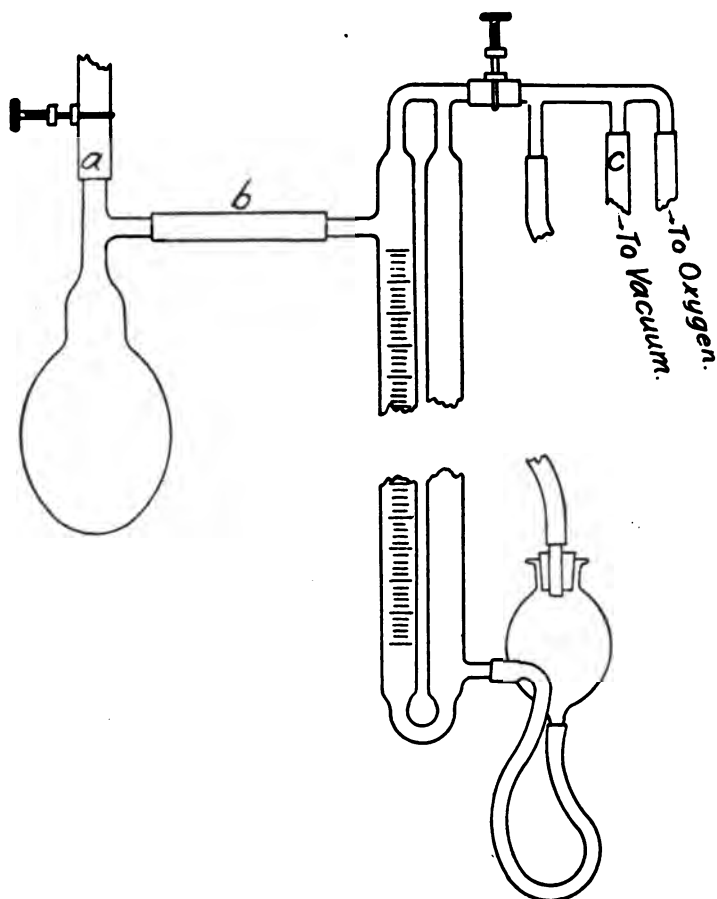
Fig. 1.

connected with the gas-burette. The flask is carried in a holder (Fig. 2). The rods of the holder, *a a'* (Fig. 2), pass through holes, *a a'* (Fig. 3), in a brass plate which is soldered to a brass rod which may be held in the clamp of an ordinary ring stand. The manner of setting up the whole apparatus is indicated in Fig. 4, in which the whole device is shown in the thermostat. The string, *s*, is connected with the crank of a motor, by whose first half-revolution the carrier and flask are pulled from the position of rest (indicated by solid lines) to that indicated by the dotted lines. During the second half-revolution of the motor-
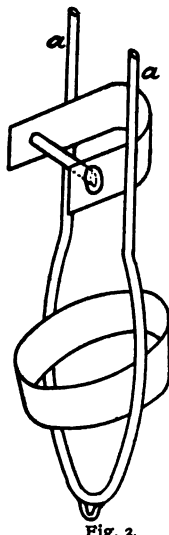
Fig. 2.
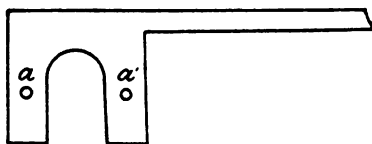
Fig. 3.
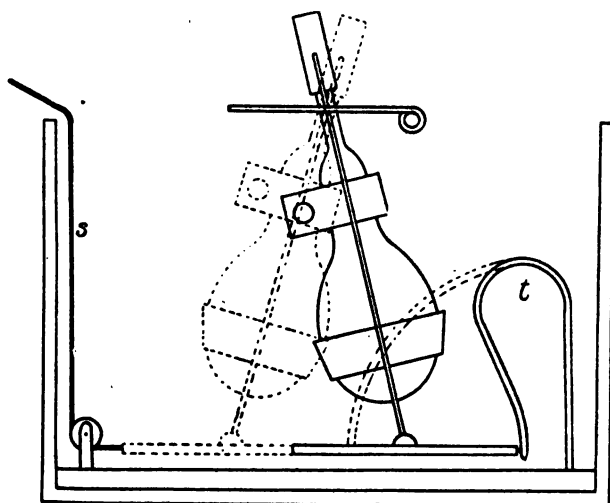
Fig. 4.

crank the strain on the string is relaxed and the flask and carrier are brought back into the original position by the ∪ shaped spring, *t*. Each revolution of the motor corresponds to one backward and forward journey of the flask. It was found that the apparatus responded readily to a rate of 400 revolutions per minute, whereas, so far as could be determined, the rate of reaction was independent of the velocity of shaking above 250 per minute, when 20 cc. of solution absorbing at the rate of not more than 2 cc. per minute were used. As will be seen from what follows, no very thorough test of the efficiency of the device is as yet possible because other accidental factors which have not as yet become avoidable have a much greater influence upon the velocity of reaction than does the rate of shaking.

In a thermostat of ordinary size the apparatus works better at high shaking rate than at slow because the waves in the thermostat are automatically broken. In using the apparatus for low shaking rates it was found necessary to provide a collar to fit around the carrier and to float upon the surface of the water in the thermostat. The collar used was about 7 inches in diameter.

The oxygen used was prepared electrolytically, using nickel electrodes and potassium hydroxide solution as electrolyte. Potassium hydroxide has the advantage over sulphuric acid, that by its electrolysis no ozone nor hydrogen peroxide is formed.[1]

The general method of procedure (with a few exceptions to be related later) was as follows :

1. The flask, after having been thoroughly cleaned and steamed out, was placed in the thermostat in the carrier. The upper outlet of the tube was provided with a piece of thick-walled rubber tubing, which could be closed with a screw-clamp. The side-tube was connected with a gas-burette (Fig. 1) and the whole apparatus thoroughly evacuated. Oxygen from the electrolytic generator was admitted until the apparatus was filled. The evacuation was then repeated and fresh oxygen allowed to enter. This whole operation was repeated a third time to insure the apparatus being filled with pure oxygen.

2. The apparatus being thus prepared, 20 cc. of the solution to be investigated were filled in through the upper opening by

1 Bodenstein : *Ztschr. phys. Chem.*, 29, 667.

means of a special device, and the corresponding volume of air allowed to escape at *c* (Fig. 1).

3. All openings were now quickly closed (except *c* which was left open to the air) and the motor started. The reading of the gas-burette usually became slightly larger for the first few seconds and then began to steadily grow smaller, owing to the absorption of oxygen by the solution. The first increase of volume is undoubtedly due to the slight evaporation of water from the solution until the vapor-pressure is reached throughout the flask.

4. After the volume has been decreasing for about ten seconds the reading of the gas-burette is taken and at the same time a stop-watch is started, and further readings are taken at convenient intervals.

5. The residual stannous chloride, after the reaction had become very slow, was titrated with standard bichromate solution, with starch and potassium iodide as indicator. In some cases where the reaction went very rapidly it was considered better to continue the experiment until no more oxygen was absorbed ; *i. e.*, until all stannous chloride had been oxidized.

The beginning concentration of stannous chloride was determined by the whole volume of oxygen absorbed and the volume of bichromate used, while the amounts of stannous chloride converted at the end of different periods were calculated from the readings on the gas-burette. Since the rate of decrease in the volume of oxygen was independent of the velocity of shaking (*i. e.*, the velocity of shaking was made so great that it had no further influence), we can place the concentration of the oxygen as constant for any series of experiments with solutions of the same compositions (if the slight correction be made for variation of the atmospheric pressure).

That with solutions of different concentrations this is probably not strictly allowable, seems to be shown by the experiments of Setschenow,[1] who found that the solubility of carbon dioxide in salt solutions decreased very considerably with increasing concentration of the salt. However, since the investigation has not yet reached a point where exact determinations are possible, this need not be taken into further consideration at present.

[1] *Ztschr. phys. Chem.*, **4**, 117.

The concentration of the hydrochloric acid in the solutions was determined by taking standardized solutions of the acid in making up the solutions for investigation. All measurements were made at 25° C.

Before relating the results of the above-described method of investigation it will be well to take into consideration a few preliminary results which were obtained by a slightly different method. This method consisted in placing an approximately weighed quantity (0.5 gram) of stannous chloride crystals into the flask of the apparatus, then filling with oxygen, adding solvent (either water or hydrochloric acid of known strength), starting the motor and making measurements from the start. Other experiments in comparison were made by allowing the so-prepared solutions to stand for considerable periods, in order that any reaction between solvent and stannous chloride might become complete. The object of these experiments was to see if the slow hydrolysis of the salt which appears to take place,[1] would have any influence upon the rate of oxidation. In this connection the following series of measurements are given : A. Measurements with 0.25 normal stannous chloride without hydrochloric acid. Experiment started immediately upon mixing of the solution. B. Measurements with some of the same solution which had stood for one hour. C. Measurements with similar solution which had stood forty-eight hours. D. Parallel with C.

In Columns T are given elapsed time in minutes, and in V the absorbed volumes of oxygen, in cubic centimeters. Columns D give volume of oxygen for each time interval.

EXPERIMENT A.

Conc. SnCl$_2$, $\frac{1}{4}$ normal.   HCl = 0.

T.	V.	D.
0	0.00	...
4	0.40	0.40
8	0.88	0.48
12	1.38	0.50
16	2.02	0.64
20	2.80	0.78
24	3.62	0.82
28	4.50	0.88
32	5.52	1.02
36	6.50	0.98

(Experiment interrupted.)

[1] This Journal, 23, 21.

EXPERIMENT B.

Conc. SnCl$_2$, $\frac{1}{4}$ normal. HCl = o. Solution 1 hour old.

T.	V.	D.	T.	V.	D.
0	0.00	...	40	10.95	1.25
4	0.80	0.80	44	12.12	1.17
8	1.75	0.95	48	13.25	1.13
12	2.72	0.97	52	14.34	1.09
16	3.80	1.08	56	15.44	1.10
20	4.90	1.10	60	16.35	0.91
24	6.05	1.15	64	17.22	0.87
28	7.25	1.20	68	17.94	0.72
32	8.45	1.20	72	18.62	0.68
36	9.70	1.25			

EXPERIMENT C.

Same solution. 48 hours old.

T.	V.	D.	T.	V.	D.
0	0.00	...	45	13.11	1.38
5	1.43	1.43	50	14.51	1.40
10	2.83	1.40	55	15.68	1.17
15	4.28	1.45	60	16.70	1.02
20	5.68	1.40	65	17.58	0.88
25	7.18	1.50	70	18.28	0.70
30	8.73	1.55	80	19.23	0.95
35	10.28	1.55	90	19.91	0.68
40	11.73	1.45	100	20.26	0.35

EXPERIMENT D.

Parallel with C, but with new solution. Also 48 hours old.

T.	V.	D.	T.	V.	D.
0	0.00	...	40	12.14	1.54
5	1.35	1.35	45	13.63	1.49
10	2.80	1.45	50	14.94	1.31
15	4.28	1.48	55	16.13	1.19
20	5.84	1.50	60	17.14	1.01
25	7.45	1.61	65	17.94	0.80
30	9.03	1.58	75	19.04	1.10
35	10.60	1.54	85	19.74	0.74

In the above experiments the solutions were prepared before placing them in the flask. In the following ones (E–H) the solutions were prepared as described above, by first placing the crystallized salt in the flask, then filling the apparatus with oxygen, adding solvent (water or dilute hydrochloric acid), and starting the motor. One-half gram stannous chloride was used which made the solution approximately $\frac{1}{4}$ normal.

EXPERIMENT E.

0.5 gram SnCl₂ + 20 cc. pure water.

T.	V.	D.	T.	V.	D.
0	0.00	...	50	13.98	1.50
5	0.70	0.70	55	15.33	1.35
10	1.61	0.91	60	16.65	1.32
15	2.95	1.34	65	17.83	1.18
20	4.51	1.56	70	18.83	1.00
25	6.03	1.52	75	19.62	0.79
30	7.66	1.63	80	20.20	0.58
35	9.24	1.58	85	20.70	0.50
40	10.88	1.64	90	21.12	0.42
45	12.48	1.60			

EXPERIMENT F.

Parallel with E.

T.	V.	D.	T.	V.	D.
0	0.00	...	50	14.60	1.50
5	0.82	0.82	55	15.98	1.38
10	1.94	1.12	60	17.22	1.24
15	3.40	1.46	65	18.32	1.10
20	4.98	1.58	70	19.22	0.90
25	6.52	1.54	75	19.95	0.73
30	8.12	1.60	80	20.54	0.59
33	9.80	1.68	85	21.00	0.46
40	11.48	1.68	90	21.35	0.35
45	13.10	1.62			

The agreement between E and F is fairly good, especially as the two portions of 0.5 gram each of stannous chloride were not weighed very exactly. Further, two or three minutes' time was accidentally lost at the beginning of F, so that all of the early readings are somewhat too large. However, the general course of the absorption corresponds very closely in both cases, and as preliminary experiments they are satisfactory.

Experiments G and H, following, were made in exactly the same way except that ½ normal hydrochloric acid was used instead of pure water in making up the solutions.

EXPERIMENT G.

0.5 gram SnCl₂ + 20 cc. ½ normal HCl. End strength = 0.80[1] cc.

T.	V.	D.	T.	V.	D.
0	0.00	...	20	7.10	1.55
5	2.13	2.13	25	8.63	1.53
10	3.95	1.82	30	10.10	1.47
15	5.55	1.60	35	11.45	1.35

[1] All titrations are expressed in terms of the number of cubic centimeters of 0.10 normal K₂Cr₂O₇.

T.	V.	D.	T.	V.	V.
40	12.70	1.25	80	20.55	0.75
45	13.87	1.17	85	21.27	0.72
50	14.99	1.12	90	21.95	0.68
55	16.07	1.08	95	22.57	0.62
60	17.06	1.02	100	23.16	0.59
65	18.07	0.98	105	23.72	0.56
70	18.95	0.88	110	24.22	0.50
75	19.80	0.85	115	24.65	0.43

EXPERIMENT H.

0.5 gram $SnCl_2$ + 20 cc. $\frac{1}{2}$ normal HCl. End strength = 2.2 cc.

T.	V.	D.	T.	V.	D.
0	0.00	...	55	15.75	1.09
5	1.87	1.87	60	16.77	1.02
10	3.52	1.65	65	17.72	0.95
15	4.96	1.44	70	18.62	0.90
20	6.63	1.67	75	19.44	0.82
25	8.18	1.55	80	20.18	0.74
30	9.62	1.44	85	20.90	0.72
35	11.00	1.38	90	21.58	0.68
40	12.28	1.28	95	22.26	0.68
45	13.50	1.22	100	22.87	0.61
50	14.66	1.16			

Here, again, is fair agreement, although the absorption was noticeably faster in G than in H. The most noticeable feature is that in these experiments, with $\frac{1}{2}$ normal hydrochloric acid, the increase of the rate of absorption for the first thirty or forty minutes, so noticeable in the previous experiments, has disappeared. The absorption per five minutes falls off from the start to the finish of the reaction.

The approximate agreement of the results of parallel experiments by the above method permits of the hope of determining the true reaction velocity between oxygen and stannous chloride solutions, by some refinement of the above method. From this point on, a modification of the above method was introduced. By this method a considerable quantity of a solution $\frac{1}{2}$ normal as to hydrochloric acid and $\frac{1}{4}$ normal as to stannous chloride, was prepared. This was filled into carefully cleaned tubes of about 80 cc. capacity, sealed up after thorough evacuation, and allowed to stand until wanted. In making a series of measure-

ments a tube was opened, a portion taken out, the tube then
closed with a piece of thick-walled rubber tubing, and evacuated
again, and thus kept until another portion was wanted. Contrary
to expectations, this method gave extraordinarily irregular
results, the variation between the rates of oxidation of two por-
tions taken from the same tube being sometimes as great as several
hundred per cent. The results of a number of measurements
made by this method are given below. There are also given in
some cases the velocity constants of the reaction calculated upon
the basis that the concentration of the stannous chloride is the
only one that changes during the reaction (*i. e.*, assuming that
the oxygen concentration is constant and that the products of the
reaction exert no catalytic action). In many cases only the read-
ings for the first few minutes are given because it was not con-
sidered necessary to complete each experiment when varying
results were obtained. Experiments I$_a$, I$_\beta$, and I$_\gamma$ were made
with one and the same solution. I$_a$ and I$_\beta$ were about two hours
apart, while I$_\beta$ and I$_\gamma$ were about twenty-four hours apart. All
following experiments were made with $\frac{1}{2}$ normal HCl and $\frac{1}{5}$ nor-
mal SnCl$_2$ solutions.

EXPERIMENT I$_a$.

End strength = 0.90 cc.   A = 0.2008.

T.	V.	D.	X.	$\dfrac{\log \frac{A}{A-X}}{T} = K.$
0	0.00	...	0.00000	....
5	3.60	3.60	0.02925	0.01370
10	6.65	3.05	0.05405	0.01362
15	9.30	2.65	0.07558	0.01367
20	11.45	2.15	0.09296	0.01350
25	13.30	1.85	0.10810	0.01346
30	14.95	1.65	0.12150	0.01348
35	16.42	1.47	0.13350	0.01359
40	17.80	1.38	0.14460	0.01382
45	19.00	1.20	0.15460	0.01418
50	19.98	0.98	0.16240	0.01439
55	20.80	0.82	0.16900	0.01455
60	21.65	0.85	0.17600	0.01530
65	22.40	0.75	0.18200	0.01582
70	23.05	0.65	0.18730	0.01675
75	23.60	0.55	0.19180	0.01798

EXPERIMENT Iβ.

A = 0.2008.

T.	V.	D.	X.	$\dfrac{\log \frac{A}{A-X}}{T} = K.$
0	0.00	...	....	....
5	4.80	4.80	0.03900	0.01876
10	9.05	4.25	0.07353	0.01979
15	12.50	3.55	0.10160	0.02041
20	15.25	2.75	0.12390	0.02084

EXPERIMENT Iγ.

End strength = 1.10. A = 0.1998.

T.	V.	D.	X.	$\dfrac{\log \frac{A}{A-X}}{T} = K.$
0	0.00	...	....	....
5	4.70	4.70	0.03735	0.01802
10	8.70	4.00	....	....
15	11.98	3.28	....	....
20	14.52	2.54	0.11530	0.01870
27	17.40	1.98	....	....
30	18.40	1.00	....	....
35	19.88	1.48	....	....
40	21.15	1.27	0.16810	0.02000
45	22.25	1.10	....	....
50	23.12	0.87	....	....
55	23.80	0.68	....	....
60	24.40	0.60	0.1938	0.02540

It will be noticed that in each of these last three series of measurements the rate of oxidation is very considerably greater than with solutions of the same concentration, but which were prepared in the flask of the shaking apparatus (Experiments G and H). In fact the rate is more than doubled. It would thus seem that the rate of oxidation of the solution increases with its age to a certain extent. The same may be noticed by comparison of Experiments A, B, C, and D.

Another very marked regularity among the irregularities was noticed. The phenomenon may be briefly described, as follows: If a tube of the fresh solution were opened and allowed to stand for about twenty minutes in the air, different portions of the solution gave results in approximate agreement. But if care were taken not to open the tube until immediately before an experiment, and then to transfer the first portion immediately into the appa-

ratus, this first portion invariably gave results much higher than succeeding portions, and the succeeding portions again gave results agreeing fairly well. The following two experiments illustrate the falling off in the rate of oxidation after the tube with solution had stood for a few moments exposed to the air. Measurements α are with first portions, taken as soon as possible after opening the tube. Measurements β are taken about one-half to one and one-fourth hours later. The influence of oxidation by the air on standing thus long was not significant, as the solutions gave practically the same concentrations of stannous chloride for β-measurements as for α-measurements.

EXPERIMENT Jα.

T.	V.	D.	T.	V.	D.
0	0.00	...	20	13.80	2.40
5	4.50	4.50	25	15.80	2.00
10	8.24	3.74	30	17.75	1.95
15	11.40	3.16	35	19.45	1.70

EXPERIMENT Jβ.

T.	V.	D.	T.	V.	D.
0	0.00	...	50	21.00	1.10
5	3.32	3.32	55	22.20	1.20
10	6.40	3.08	60	23.22	1.02
15	9.20	2.80	65	24.18	0.96
20	11.65	2.45	70	25.00	0.82
25	13.80	2.15	75	25.70	0.70
30	15.80	2.00	80	26.10	0.40
35	17.40	1.60	85	26.30	0.20
40	18.75	1.35	90	26.45	0.15
45	19.90	1.15			

EXPERIMENT K (α AND β).

Kα.			Kβ.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
5	6.52	6.52	5	2.56	2.56
10	11.70	5.18	10	4.80	2.24
15	15.50	3.80	15	6.90	2.10
20	18.40	2.90	20	8.80	1.90
25	20.52	2.12	25	10.50	1.70
30	22.20	1.78	30	12.00	1.50
35	23.50	1.30	35	13.50	1.50

It was thought possible that the reaction in question might be sensitive to the influence of light and a very considerable number

of experiments were carried out to determine whether or not this was the case. The results of the investigation showed clearly that if light had any influence upon the rate of reaction, it was so small as to be insignificant in comparison to other disturbing factors. It will scarcely be necessary to relate these experiments in detail here, as the results are purely negative.

On account of the fact that a solution that had been preserved *in vacuo* for some time experienced a considerable fall in oxidation rate on exposure to the air for a few moments, it was thought possible that the re-evacuation of the tube might remove at least partially the agent which brought about the depression in the oxidation rate. Several experiments were carried out to determine this. The re-evacuation had no apparent influence, as the following measurements show. Only the volumes absorbed in the first five minutes are given. Under "α" are the values for the first portions, taken immediately upon opening the tube ; under "β" the values taken after the solution had stood for some little time exposed to the air (usually with one or two shakings) ; under "γ" are the results after the solutions had been re-evacuated, and had remained sealed up from four to eighteen hours.

No.	α.	β.	γ.
1	6.00	3.70	3.43
2	7.50	4.20	3.25
3	6.85	4.20	4.10
4	9.00	5.00	5.30

In No. 4 a small increase in γ over β is observed. Otherwise the γ-values are regularly smaller than the β-ones. This is probably due to the effect that after β-portions were taken out it was necessary to allow the tube to stand open for a few moments longer before re-evacuation.

As a result of the above measurements, we may draw the conclusion that the reaction between stannous chloride solutions and oxygen is extremely sensitive to minute quantities of substances with which the reagents may come in contact in the ordinary, careful methods of laboratory manipulation.

The investigation was at this point turned toward the determination of these disturbing actions, and considerable headway has already been made in this direction. Before relating the results of this part of the investigation, however, it may be well

to consider the results of the measurements already given from a somewhat critical standpoint. In the following table a summary

is given of the values of $\dfrac{\log \dfrac{A}{A-X}}{T}$ for several series of meas-

urements. The values are determined from the data of solutions of practically equal concentrations; *viz.*, 0.2 normal. Constants calculated for five minute differences.

					Experiments not given in the foregoing.		
Expt. E.	**Expt. H.**	**Expt. Ia.**	**Expt. Iy.**	**Expt. Ka.**			
1.	2.	3.	4.	5.	6.	7.	8.
0.00244	0.00666	0.01370	0.01802	0.02432	0.01120	0.01150	0.0230
0.00284	0.00633	0.01362	....	0.02506	0.01158	0.01175	....
0.00356	0.00625	0.01367	....	0.02516	0.01200	0.01217	....
0.00424	0.00652	0.01350	0.01870	0.02539	0.01239	0.01219	0.0222
0.00466	0.00670	0.01346	....	0.02550	0.01217	0.01244	....
0.00516	0.00683	0.01348	....	0.02757	0.01233	0.01270	0.0252
0.00555	0.00698	0.01359	....	0.02591	0.01242	0.01287	....
0.00603	0.00711	0.01382	0.02000	0.02588	0.01266	0.01335	0.0268
0.00645	0.00724	0.01418	....	0.02940	0.01282	0.01385	....
0.00688	0.00739	0.01439	....	0.03252	0.01317	0.01381	0.0310
0.00724	0.00756	0.01455	....	0.03040	0.01356	0.01451	0.0306
0.00764	0.00771	0.01530	0.02540	0.03040	0.01403	0.01536	0.0310
0.00802	0.00788	0.01582			0 01464		
0.00830	0.00808	0.01675					
0.00846	0.00827	0.01798					
0.00850	0.00845						
0.00850	0.00868						
0.00846	0.00897						
	0.00935						
	0.00975						

Column 1 is for an experiment made without hydrochloric acid and by mixing the solution in the apparatus and starting the experiment immediately. On the assumption that the reaction is simply proportional to the analytically determined concentration of stannous chloride these numbers should be constant. They increase, however, to a value at the end of the experiment which is nearly four times its original value. The values in Column 2

are for an exactly similar experiment, made, however, with 0.5 normal hydrochloric acid instead of pure water. The values here show the same sort of an increase except that it is much less marked. The remaining values are all for experiments made with solutions containing 0.5 normal hydrochloric acid and kept sealed up in vacuum tubes for from twenty-four hours to one week before using. It will be noticed that all columns show marked increase from the beginning to the end values, and, with the exception of a few scattered values (presumably experimental errors), this increase is fairly regular. A further regularity will be noticed also in that the ratio between the first and last values of a column is approximately the same for all columns (excepting Column 4, which may be due to an experimental error ; in my note-book I find that the determination of the end reaction in this case was doubtful). In other words, although the actual values of the velocity constants vary greatly in different series, the increase in a given series is approximately proportional to the change in concentration for solutions of the same concentration in hydrochloric acid. In solutions made without hydrochloric acid the ratio of increase is very much larger, and may be so large that it causes an actual increase in the volume of oxygen absorbed with decreasing (analytical) concentration of stannous chloride (Experiments A, B, C, D, E, and F). The simplest explanation of this would be that some product of the reaction acts as an accelerator of the reaction. The products we should naturally look for are hydrochloric acid, stannic hydroxide, and stannic chloride, one or more of which might be formed. The reaction may take place as follows :

$$SnCl_2 + 3H_2O + O = Sn(OH)_4 + 2HCl. \qquad (1)$$
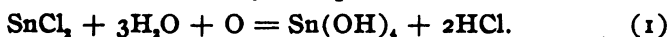
It is well known that in moderately dilute solutions stannic chloride is almost completely hydrolyzed, and this might lead one to expect that the hydrolyzed system would be formed under the conditions of these experiments. However, according to the Ostwald rule[1] it happens very generally that, as the product of a reaction, not the most stable, but rather some intermediately stable product, is formed. If the rule held in this case, we should get stannic chloride formed as first product according to the equation :

$$SnCl_2 + 2HCl + O = SnCl_4 + H_2O. \qquad (2)$$

[1] *Ztschr. phys. Chem.*, **22**, 306.

and the stannic chloride would then slowly hydrolyze :

$$SnCl_4 + 2H_2O = Sn(OH)_4 + 4HCl. \qquad (3)$$
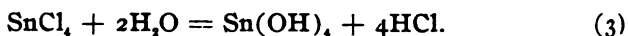
The only experimental evidence bearing upon this point that I have found is the following :

Thomsen[1] found that when stannous chloride solutions were oxidized with free chlorine, they showed a strong yellow color. This yellow color is also shown when an old solution of stannic chloride is mixed with stannous chloride. The solution must be some days old to give a distinct color. This color reaction is taken by Thomsen[2] as a test for the "metastannic" condition. At any rate, the color is evidence of a condition in the stannic solution which appears only after long standing of its solution. In the foregoing work it was noticed that after an experiment the oxidized solution was invariably yellow and the yellow color was deeper in solutions which contained less free hydrochloric acid. This would indicate that the stannic chloride stage in this reaction was passed by and the reaction took place according to equation (1). The point cannot, however, be looked upon as definitely settled as yet. The matter is open to direct determination by electrolytic methods, and this will be done in the near future.

The course of the reaction has an important bearing on the theoretical considerations concerning the reaction velocity. If the reaction takes place according to equation (1) we can place the increase in concentration of hydrochloric acid directly proportional to the decrease in concentration of stannous chloride. If the reaction takes place according to equations (2) and (3) we should have to set the increase in hydrochloric acid as a function of the velocity of oxidation of stannous chloride and of the velocity of hydrolysis of the stannic chloride formed. That hydrochloric acid acts as an accelerator in some way cannot be doubted since the solutions made with $\frac{1}{4}$ normal hydrochloric acid give constants from three to ten times as large as those made with water. If the reaction takes place according to equation (1), the fact that hydrochloric acid acts as an accelerator allows of a ready explanation of all the peculiarities noticed in the different series

of values of $\dfrac{\log \dfrac{A}{A-X}}{T}$ except the lack of agreement among the

1 " Thermochemische Untersuchungen," Vol. II, p. 445.
2 Thomsen : *Loc. cit.*

different series, which matter will be discussed later.   Assuming
that the reaction takes place according to equation (1), an
increase in the concentration of the hydrochloric acid must occur.
The first effect of this hydrochloric acid will be to drive back
hydrolysis, if notable hydrolysis exist in the solution.   If we con-
sider that the hydrolyzed portion of the stannous chloride has a
lower oxidation rate than unhydrolyzed stannous chloride (or
that it is not directly oxidizable at all),[1] it would necessarily fol-
low that the activity of a stannous chloride solution made with
water would increase as the oxidation proceeded, since more and
more of the hydrolyzed product would be converted into unhy-
drolyzed.   This would take place at all concentrations of hydro-
chloric acid at which noticeable hydrolysis occurred.   The fact
that the velocity constants for solutions in 0.5 normal hydrochlo-
ric acid still show a marked increase, might be taken as evidence
that hydrolysis is still noticeable at that concentration, or it may
be that the hydrochloric acid has other accelerating influences
aside from the mere pushing back of the hydrolysis.   It is also
possible that the molecular complexes of stannous chloride and
hydrochloric acid have a greater rate of oxidation than the sim-
ple substances.

   If the reaction takes place according to equations (2) and (3),
the explanation of the facts is not so simple.   The first effect of
the oxidation will then be to form stannic chloride at the expense
of stannous chloride and hydrochloric acid ; and secondly, this
stannic chloride will begin to slowly hydrolyze.[2]   Thus, during
the first part of the reaction we shall have two increasing concen-
trations ; viz., stannic chloride and stannic hydroxide, while the
concentration of hydrochloric acid will decrease, if the hydroly-
sis of stannic chloride is very slow compared to its rate of forma-
tion.   Somewhere during the reaction stannic chloride will, on
account of its being more and more slowly produced, cease to
increase in concentration, and will, on account of continuous
hydrolysis, begin to decrease.   If the rate of oxidation of
stannous chloride is much faster than the rate of hydrolysis of

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[1] An experiment with colloidally suspended stannous hydroxide nearly free from
hydrochloric acid showed an extraordinarily slow rate of oxidation, which became very
fast upon addition of a few drops of potassium hydroxide solution.   This cannot be taken
as a wholly satisfactory determination of the above point, since it does not necessarily fol-
low that all hydrolyzed stannous salt is held in the solution in colloidal form.

[2] Kohlrausch : Ztschr. phys. Chem., 33, 257.

14-23

stannic chloride, the latter reaction must go on after the former is practically complete. This hydrolysis is measurable by electrolytic methods[1] and thus we have a possible means of determining whether or not the reaction takes place in this second way or not. These measurements will be made in the near future. Of course it is by no means excluded that stannic chloride and stannic hydroxide may act as accelerators.

Another wholly different explanation of the whole matter is possible. It may be that it is an error to assume that the reaction rate is directly proportional to the concentration of the stannous chloride. It might be proportional to some other power of the concentration than the first (*i. e.*, to C^2 or to C^3, etc.). Such cases are not unknown, apparently. In this case the values of the exponent v may be calculated from the changes in concentration during the reaction, by the well-known equation of van 't Hoff :[2]

$$ n = \frac{\log \left(\dfrac{dc_1^2}{dT_1} : \dfrac{dc_2}{dT_2} \right)}{\log (c_1 : c_2)}. $$

If the reaction took place in a perfectly uniform manner, *i. e.*, in such a manner that no accelerating or retarding influences were developed during the reaction, these values of n should be constant. I have calculated n for some few cases, and the results obtained are as follows :

A.	B.
0.464	0.435
0.433	0.412
0.401	0.355
0.372	0.320
0.337	0.270
0.293	
0.242	

The values are by no means constant, but show a marked and invariable (several sets were calculated) tendency to decrease. Thus it seems necessary to conclude that during the course of the reaction accelerating influences are developed. These influences can not be named catalytic nor autocatalytic, because they may be

[1] Kohlrausch : *Loc. cit.*

[2] See van 't Hoff : "Vorlesungen," Vol. I, p. 194 ; also Ostwald : "Lehrbuch," II, 2, p. 232.

apparently of such a nature as to change the whole equilibrium existing in the solution.

It is perfectly evident from the foregoing that before any thoroughly satisfactory explanation of the phenomena above described can be obtained, it will first be necessary to be able to control the reaction so that constant results may be obtained under a given set of conditions. It has already been suggested that the reaction seemed to be extraordinarily sensitive to the influence of small quantities of substances which it was apparently able to take up from the air on a few minutes' exposure. In Part II is given the results of an (almost purely qualitative) investigation into the cause of the great variations which were found to occur in different series of measurements under apparently like conditions. As will be seen, the phenomena of variation are readily explained, although at present the method of wholly avoiding such disturbances or even of studying them with any considerable degree of quantitative accuracy, has not been found.

PART II. CATALYTIC PHENOMENA IN THE OXIDATION OF STANNOUS CHLORIDE BY OXYGEN.

As has been stated in the previous portion of this paper, the influence of light and of re-evacuation of tubes upon the rate of oxidation of stannous chloride solutions seems to be nothing. It was now further attempted to determine the influence of other substances which could possibly come in contact with the solution. The first substance investigated was rubber. Since portions of the apparatus were made of rubber tubing, it was thought that the fact that the solution came (or might come) in contact with the rubber, could possibly exert some influence. The method of procedure was as follows : The rubber tubing was rubbed to a fine powder by means of a clean file. From 0.25 to 0.5 gram of this powder was placed in the tube containing the solution to be investigated, and the tube sealed off and rotated in the thermostat for about eighteen hours. The solution was tested as to its oxidation rate before and after the addition of the rubber. The results of two such experiments are given in the following table. Under α are the values for T, V, and D before addition of rubber, and under β the same values after the addition :

TABLE I.

Experiment 1.

a.			β.		
T.	V.	D.	T.	V.	D.
o	0.00	...	o	0.00	...
5	4.35	4.35	5	11.20	11.20
10	8.32	3.97	10	22.20	11.00
15	11.90	3.58	13	26.20	4.00

Experiment 2.

a.			β.		
T.	V.	D.	T.	V.	D.
o	0.00	...	o	0.00	....
5	4.70	4.70	5	18.20	18.20
10	9.05	4.35	10	25.60	7.40
15	12.85	3.80			

As will readily be seen, the influence of the rubber is that of a wonderfully active accelerator, the acceleration in the first case being over 150 per cent. and in the second nearly 300 per cent. Thinking that possibly the sulphur in the rubber might be the active agent in bringing about this acceleration, experiments were carried out in the same way as those with rubber, using sulphur instead of the rubber. The sulphur used was the ordinary crystallized sulphur ground up to a fine powder. The tube with solution and sulphur was rotated in the thermostat as in the case of rubber, for about eighteen hours.

In Table II are given the results of one of these experiments, the results in all being of the same nature. Under α results before and under β results after addition of sulphur :

TABLE II.

a.			β.		
T.	V.	D.	T.	V.	D.
o	0.00	...	o	0.00	...
5	3.30	3.30	5	9.95	9.95
10	7.40	3.10	10	18.10	8.15
15	9.20	2.80	15	24.90	6.80

Here there is noticed a similar acceleration to that brought about by rubber, and the value of it is about 200 per cent. The influence of sulphur and rubber is evidently one which gradually develops in the solution, since experiments which were started with simple solution were not noticeably influenced by dropping in bits

of rubber or of sulphur during the experiment. The effect appears first after the solution and the accelerator have stood together for some time. Thus it is evident that the phenomenon is due either to slow solution of the accelerator or to a slow chemical reaction between the substance and the solution.

Solutions of iron, copper, manganese, and chromium salts were next qualitatively investigated. The method was to take a portion of a solution, measure its initial velocity, then add a few drops of the dilute solution of the salt in question, and continue the experiment. By noting the rate of absorption before and after the addition of the salt solution it was possible to determine whether the addition had any considerable influence. There was no attempt made to determine the quantity of salt added. Three or four drops of the ordinary laboratory solutions were used. Following, in Table III, are the results. The values in parentheses indicate the points at which the addition of the salt solution was made :

<div align="center">TABLE III.</div>

FeSO₄.			CuSO₄.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
5	2.80	2.80	1	0.90	0.90
(5)	(2.80)	...	2	1.85	0.95
10	10.90	8.10	3	2.80	0.95
			(3)	(2.80)	...
			4	5.30	2.50
			5	7.30	2.00
			6	9.20	1.90
			7	10.90	1.70
			8	12.40	1.50

MnSO₄.			Cr₂(SO₄)₃.		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	1.00	1.00	1	0.72	0.72
2	2.00	1.00	2	1.40	0.68
3	2.90	0.90	3	2.20	0.80
(3)	(2.90)	...	4	3.10	0.90
4	3.65	0.75	5	4.05	0.95
5	4.35	0.70	(5)	(4.55)	..
6	5.05	0.70	6	5.33	·0.78
7	5.75	0.70	7	6.20	0.87
			8	7.05	0.85
			9	7.95	0.90

Thus iron and copper both cause very notable accelerations, manganese a slight retardation, while the results for chromium are somewhat irreguiar and leave us in doubt. The influence of chromium would appear at best to be very slight.

Up to this point it will be observed that all catalysors[1] studied are positive (*i. e.*, accelerating), or very weakly negative, in their action, while in the experiments related in Part I it is evident that one or more negative catalysors were at work (see Experiments J and K.

It was thought likely, as the rate of oxidation of the solution kept in evacuated tubes became considerably reduced upon the opening of the tube, that some constituent of the air might cause the variations. It was my custom to smoke freely in the room in which the work was being done, and it occurred to me that this might possibly be the cause of the trouble. In the following table (IV) are contained the results of an experiment to determine this point. Under α are the values for a clean, fresh solution, taken directly from the tube, and under β corresponding values for the same solution through which tobacco smoke had been blown.

TABLE IV.

\(\alpha\).			\(\beta\).		
T.	V.	D.	T.	V.	D.
0	0.00	...	0	0.00	...
1	1.00	1.00	1	0.30	0.30
2	1.90	0.90	2	0.60	0.30
3	2.85	0.95	3	0.95	0.35
4	3.80	0.95	4	1.28	0.33
			5	1.60	0.32
			10	3.13	1.53
			15	4.55	1.42

In Table V are the results of a series of readings taken upon a solution by the same method as was used in investigating the metallic salts (above Table III), except that instead of solution of metallic salts a few drops of an extract of tobacco were added.

[1] I use the word 'catalysor' as equivalent to the German word 'Katalysator.' It is much less cumbersome than the usual terms "catalytic agent" and "contact agent."

TABLE V.

T.	V.	D.	
o	0.00	...	
I	1.45	1.45	
2	2.90	1.45	
3	4.38	1.48	
(3)	(4.38)	...	(extract added)
4	4.80	0 42	
5	5.20	0.40	
6	5.60	0.40	
7	6.03	0.43	

These results leave not a shadow of doubt but that both tobacco smoke and tobacco extract retard the oxidation rate of stannous chloride to a high degree. The next experiments were carried out with a number of common alkaloids and with a variety of other substances, including aniline and alcohol. The results are given in Table VI.

TABLE VI.

$1/1000$ Normal brucine.			$1/200$ Normal brucine.		
T.	V.	D.	T.	V.	D.
o	0.00	...	o	0.00	...
I	1.25	1.25	I	2.38	2.38
2	2.50	1.25	(I)	(2.38)	...
3	3.75	1.25	2	3.00	0.62
(3)	(3.75)	...	3	3.56	0.56
4	4.75	1.00	4	4.06	0.50
5	5.75	1.00	5	4.55	0.50
6	6.75	1.00	6	5.04	0.48

$1/150$ Normal morphine.			$1/200$ Normal morphine.		
T.	V.	D.	T.	V.	D.
o	0.00	...	o	0.00	...
I	3.55	3.55	I	1.40	1.40
(I)	(3.55)	...	(I)	(1.40)	...
2	4.35	0.80	2	2.10	0.70
3	5.10	0.75	3	2.85	0.75
4	5.83	0.73	4	3.55	0.70
5	6.55	0.72	5	4.20	0.65
6	7.15	0.60			

$1/250$ Normal nicotine.			$1/25$ Normal nicotine.		
T.	V.	D.	T.	V.	D.
o	0.00	...	o	0.00	...
I	1.82	1.82	I	1.50	1.50
2	3.65	1.83	2	2.80	1.30
(2)	(3.65)	...	(2)	(2.80)	...
3	5.15	1.50	3	3.60	0.80
4	6.45	1.30	4	4.40	0.80
			5	5.20	0.80

$1/_{250}$ Normal phenol.		
T.	V.	D.
0	0.00	...
1	1.25	1.25
2	2.40	1.15
(2)	(2.40)	...
3	3.75	1.35
4	5.05	1.30

$1/_{25}$ Normal phenol.		
T.	V.	D.
0	0.00	. .
1	1.35	1.35
2	2.65	1.30
(2)	(2.65)	...
3	3.90	1.25
4	5.05	1.15
5	6.15	1.10

$1/_{200}$ Normal aniline.		
T.	V.	D.
0	0.00	...
1	1.55	1.55
2	3.10	1.55
(2)	(3.10)	...
3	4.05	0.95
4	5.00	0.95

$1/_{40}$ Normal aniline.		
T.	V.	D.
0	0.00	...
1	0.95	0.95
2	1.90	0.95
(2)	(1.90)	...
3	2.25	0.35
4	2.60	0.35
5	2.90	0.30

$1/_{200}$ Normal aniline.		
T.	V.	D.
0	0.00	...
1	1.30	1.30
2	2.55	1.25
3	3.90	1.30
(3)	(3.90)	...
4	4.70	0.80
5	5.50	0.80

$1/_{40}$ Normal aniline.		
T.	V.	D.
0	0 00	...
1	0.80	0.80
2	1.60	0.80
(2)	(1.60)	...
3	1.90	c.30
4	2.20	0.30
5	2.50	0.30

$1/_{200}$ Normal pyridine.		
T.	V.	D.
0	0.00	...
1	1.40	1.40
2	2.80	1.40
(2)	(2.80)	...
3	4.40	1.60
4	5.90	1.50

$1/_{40}$ Normal pyridine.		
T.	V.	D.
0	0.00	...
1	1.60	1.60
2	3.10	1.50
(2)	(3.10)	...
3	4.30	1.20
4	5.30	1.00
5	6.35	1.05

$1/_{100}$ Normal KCN.		
T.	V.	D.
0	0.00	...
1	1.07	1.07
2	2.15	1.08
3	3.23	1.08
(3)	(3.23)	...
4	4.03	0.80
5	4.83	0.80
6	5.65	0.82

$1/_{20}$ Normal KCN.		
T.	V.	D.
0	0.00	...
1	0.80	0.80
2	1.60	0.80
3	2.42	0.82
(3)	(2.42)	...
4	2.74	0.32
5	3.15	0.41
6	3.52	0.37

$\frac{7}{100}$ Normal ethyl alcohol.			$\frac{7}{10}$ Normal ethyl alcohol.		
T.	V.	D.	T	V.	D.
0	0.00	...	0	0.00	...
1	2.30	2.30	1	0.45	0.45
(1)	(2.30)	...	2	0.90	0.45
2	5.80	3.50	3	1.35	0.45
3	8.70	2.90	4	1.80	0.45
4	11.45	2.75	(4)	(1.80)	...
5	13.80	2.35	5	2.80	1.00
6	15.50	1.70	6	3.55	0.75
			7	4.25	0.70
			8	5.00	0.75

A single test was also made with mannite which retards the reaction to a considerable extent, but as the concentration of the mannite used was not known, figures are not given. The experiments were carried out in the same way as those with metallic salts, and the numbers in parentheses indicate the point at which the foreign substance was added. In most cases where experiments with two concentrations were made they were both made in the same solution, the effect of the foreign substance in the more dilute form being first observed, after which a second portion of the foreign substance was added sufficient to give the solution the greater concentration. Thus the figures for greater concentrations do not give a really fair idea of the total influence of the foreign substance, because the oxidation rate in such cases had already been considerably influenced by the previous small addition. Further no attempt was made to determine accurately the concentration of the foreign substances added, although the values are probably correct to within 5 per cent. There was no object in attempting greater accuracy, because the initial rates could not be controlled to within less than from 50 to 100 per cent.

Finally there remains to be related the results of a series of experiments made with hydrogen sulphide. A solution of hydrogen sulphide was prepared in the usual way and diluted with thoroughly boiled water to the concentration desired. One cc. of such solution was added to stannous chloride solutions during the progress of their oxidation. Since always 20 cc. portions of stannous chloride solution were used, the concentration of the stannous sulphide formed in the whole solution could be calculated readily, on the assumption that the reaction

$$SnCl_2 + H_2S = SnS + 2HCl$$
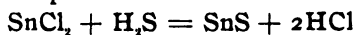
is a complete one. In Table VII are given the results of such determinations. The first column gives the concentration of the stannous sulphide in the solution. The second column gives the rate of oxidation in cubic centimeters of oxygen per minute *before* the addition of the hydrogen sulphide. The third column gives the value of the same *after* addition. The fourth column gives the ratios between the third and the second columns ; *i. e.*, the number of times faster the reaction goes after than before the addition.

The concentrations in the first column are given in terms of normality of hydrogen sulphide, considering this substance to be a monobasic acid.

<div align="center">TABLE VII.</div>

I. C_{H_2S}.	2. Rate before. cc.	3. Rate after. cc.	4. $\dfrac{\text{Rate after}}{\text{Rate before}}$.
$\frac{1}{1000}$ N	1.30	11.50	8.80
$\frac{1}{5000}$ N	0.73	7.40	10.00
$\frac{1}{10000}$ N	1.35	5.70	4.20
$\frac{1}{25000}$ N	1.00	3.50	3.50
$\left\{ \frac{1}{50000} \text{ N} \right.$	1.00	1.30	$1.30 \Big\}$
$\left. \frac{1}{50000} \text{ N} \right.$	1.20	1.45	$1.20 \Big/$

It will be seen that we have here a case of enormous acceleration of the rate of reaction due to exceedingly minute concentrations of the accelerating agent. For the greatest concentration given ($\frac{1}{1000}$ normal) the rate is lower than for a fifty-times more dilute solution. This is possibly due to the fact that in this case the stannous sulphide precipitated out in fine particles of the black form, while in the others (where visible at all) it was in the form of the colloidal, brownish sulphide, which separated only very slowly from the solution.

<div align="center">DISCUSSION OF THE RESULTS.</div>

It is evident from the results in Part II of this paper that we have in the reaction between stannous chloride solutions and oxygen, a reaction that is exceedingly sensitive to the influence of catalytic agencies. It is not my purpose to enter into any considerable discussion of these results here. Such discussion would be practically useless at this time, and a further investigation of the whole matter is what is most necessary. I merely wish to

call attention to what few relationships may be found between these results and the results of previous investigators. As has been seen, a very considerable number of the reagents examined decrease the rate of the reaction ; *i. e.*, act as negative catalysors, while others accelerate. As negative catalysors we find : Salts of manganese and chromium (not very active), some constituents of tobacco smoke and extract, brucine, morphine, nicotine, mannite, aniline, and potassium cyanide. As positive catalysors were found : Rubber, sulphur, hydrogen sulphide (stannous sulphide), salts of iron and copper, and alcohol. Pyridine and phenol do not exert a sufficiently strong influence to allow any decided conclusion to be drawn as to their action at present. Mannite acts negatively, but how strong its action may be is not yet determined.

Taking up the negative catalysors first, it is to be remarked that Bigelow[1] found considerable variations in the rate of oxidation of sodium sulphite by air, some of which (impurities in the air, etc.) could be at least partially controlled. His results as to the action of mannite, which was the most carefully studied agent, seem to be comparable to the results stated above. It will be noticed that most of the negative catalysors which I have found are poisons. This may very likely be due to the fact that nothing much but poisons were studied. The action of the alkaloids was investigated because of the accidental discovery that tobacco smoke was a very active agent. It is quite likely that this negative catalytic action upon the reaction is in no way characteristic of poisons. It is, however, to be remarked that Bredig and Müller von Berneck[2] found that poisons were often very active agents in destroying the catalytic action of colloidal platinum solutions.

Among the positive catalysors are found salts of copper and iron. These are already known as strong agents in this respect. The appearance of alcohol among these accelerators is quite anomalous. One would naturally expect that its influence in pushing back the dissociation of the solution would cause it to retard the reaction. But if it pushes back the dissociation it will also push back the hydrolysis and might thus hasten the reaction. The value for its influence, however, is so large

[1] *Ztschr. phys. Chem.*, **26**, 493.
[2] *Ibid.*; **31**, 258.

that it seems to me likely that its action is due to wholly other causes. Bigelow[1] found alcohol to retard the oxidation of sodium sulphite in a high degree.

The three remaining accelerators—rubber, sulphur, and hydrogen sulphide—all contain sulphur. The first two exert their influence upon the solution only after long standing, while hydrogen sulphide acts immediately.

These facts allow of a formulation of a working hypothesis, by means of which the action of all three may be ascribed to a common agent, *viz.*, stannous sulphide. Stannous sulphide is formed when hydrogen sulphide is introduced into a solution of stannous chloride. If we consider that the reaction between water and sulphur is an appreciable one, *viz.*,

$$2H_2O + 2S \; \rightleftharpoons \; 2H_2S + O_2,$$

we can account readily for the formation of stannous sulphide through the action of either rubber or sulphur. This should be susceptible of experimental determination.

It remains to be noted that Mohr, in his "Titrirmethode" (6th Ed., 1886),[2] mentions the fact that, unless great care is taken to free arsenious acid from sulphur compounds, solutions of it oxidize with great rapidity in the air. The phenomenon appears analogous to the one observed with stannous chloride.

From the results above given it would seem that a method might possibly be devised by means of which the oxidation rate of stannous chloride would be so reduced that it could be used directly as a solution for titration. If this were possible it would be of very considerable convenience for some purposes. The investigation of this point has been undertaken in the quantitative laboratory of this university.

CONCLUSION.

In Part I of this paper it is shown that the suggestion made in a previous paper[3] as to the necessity of a strict definition of the reagents in a reaction before the velocity constant or the order of the reaction can be satisfactorily determined, is not without ground. The reaction between stannous chloride solutions and oxygen is shown to undergo an acceleration during the course of the reac-

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[1] *Loc. cit.*
[2] *Loc. cit.*, p. 364.
[3] *This Journal*, **23**, 21.

tion which finds its simplest and readiest explanation in the pushing back of the hydrolysis[1] by means of hydrochloric acid produced by the reaction, and in possible catalytic action of reaction products.   In solutions free (or as free as possible) from acid this acceleration is so great that an actual increase in the rate of oxygen absorption occurs during the first part of the reaction.   It soon appears, however, that although the results of any one series of measurements are consistent within themselves and in certain ways also the results of different series are consistent with one another (*i. e.*, the ratios of initial value to end value of velocity constants are very approximately constant), nevertheless the velocity constants for different series vary within very wide limits.   This suggests the action of catalytic influences, and Part II is devoted to the detection and qualitative investigation of some of these catalytic agents.   The way for further investigation is perfectly apparent.   The first task will be to protect the stannous solutions from possible catalytic influences and to determine, if possible, the normal values for the velocity constants of the reaction with varying concentrations of hydrochloric acid, after which the influence of the various catalytic agents will be open to quantitative investigation.

The chief result of the work at present is, however, the development of an apparatus and a method by means of which reactions between liquids and gases may be readily and quantitatively studied.

The main portion of this work was carried out in the laboratory of the Physical-Chemical Institute, at Leipzig.

STANFORD UNIVERSITY,
December 11, 1900.

DETERMINATION OF SULPHUR IN WROUGHT IRON AND STEEL.

BY GEORGE AUCHY.

SEVEN or eight years ago in four samples of high carbon steels sent to two firms of commercial chemists (same drillings to each) for analysis, the sulphur was reported as follows :

	Sample No. 1.	Sample. No. 2.	Sample No. 3.	Sample No. 4.
Chemists A	0.013	0.015	0.012	0.015
" B	0.002	0.001	0.003	0.002

[1] Kortright (*Am. Chem. J.*, **17**, 116) has called attention to the probable influence of hydrolysis in the reaction between $SnCl_2$ and $FeCl_3$.

These results are interesting as illustrating the meagerness of our knowledge of our methods just a few years ago ; results such as these go to justify the sarcasm of the iron-master, who some years back declared that Ananias was the father of chemists.

In the light of our present knowledge it is easy to guess that the results of Chemists B were obtained by the aqua regia method. At that time it was customary to precipitate by the addition of 5 to 10 cc. of dilute barium chloride solution. This amount of precipitant, although adequate for high sulphur steels, utterly fails when the sulphur is very low as in the above steels, except indeed the liquid after the addition of the precipitant be evaporated to near dryness ; but since the appearance of the third edition of Blair's " Chemical Analysis of Iron," containing the recommendation to precipitate with 10 cc. of *saturated* barium chloride solution, it is extremely unlikely that such results as the foregoing have occurred.

But there is another source of error in the case of irons and low carbon steels which dissolve readily in concentrated nitric acid, well worth noting, but not spoken of in the text-books ; this source of error is the escape sometimes of the sulphur during solution in strong nitric acid. The following results illustrate how great the error may be from this cause :

| | By aqua regia method. | |
No.	As usual. Per cent.	Very slow solution. Per cent.
Iron 2456 ··········	0.006	0.012
" 2458 ··········	{ 0.006 { 0.010	0.009
" 1 ··········	0.018	0.b31
" 2 ··········	0.017	0.030
" 3 ··········	0.010	0.017
" 4 ··········	0.019	0.019
" 2459 ··········	0.006	0.015

For the results in the second column, solution was made very slowly by adding the acid very gradually, and while heating removing from the source of heat at the first appearance of red fumes, replacing after an interval, again removing at appearance of fumes, and so on, at no time allowing decided action.

In evolution methods a very important source of error is the escape of a part of the sulphur in combination with carbon.

This is a fact very well known, but almost universally ignored. In the following table of results the evolution method used was the cadmium chloride volumetric. The results of the last column were obtained in the laboratory of a large steel works. The drillings, however, were not the same as those the writer worked on, but were obtained from the same or nearly the same spot of the iron, and the results, although not strictly comparable with the writer's, nevertheless serve to show in a general way that the evolution method as carried out by the writer is not attended with any unusual source of error leading to low results, and that the error in question is a usual and common one.

In my determinations, after complete solution, the liquid was boiled till the cadmium chloride solution (in a Troilius bulb) was brought to a boil, then the flame lowered and after an interval of gentle boiling the hard boiling repeated as before.[1]

No.	By aqua regia method, slow solution. Per cent.	By evolution method. Per cent.	Another chemist's results. Per cent.
Iron 2458	0.009	0.010	....
" 1	0.031	0.019	0.013
" 2	0.030	0.018	0.012
" 3	0.017	0.009	0.012
" 4	{ 0.018, 0.019 }	0.020	0.014
" 5	0.022	0.023	0.026
" 6	0.018	0.013	0.014
" 7	0.019	0.014	0.014
" 8	0.020	0.016	0.015
" 9	....	0.014	0.013
" 10	0.021	{ 0.012, 0.016 }	0.015
" 11	0.019	0.016	0.013
" 12	{ 0.027, 0.025 }	0.014	0.014
Steel 2711	0.034	0.022	....
" A	0.018	0.018, (by another chemist).	
" B	0.020	0.020, " " "	

Steels A and B are crucible steels containing about 0.02 per

[1] At one time the writer suspected that the low results by the evolution method were due simply to insufficient boiling, and as boiling in the way described above brought higher results and results agreeing fairly well with the results by the aqua regia method this suspicion was apparently confirmed, but the rubber tube in use at that time was the white, or vulcanized kind, and it was later found that the steam carried over sulphur from the rubber tubing, apparently as hydrogen sulphide, for in a blank test a considerable yellow precipitate was seen to form.

cent. sulphur by the aqua regia method.   Five different samples
of this kind of steel tested by a commercial chemist, using the
evolution method, gave about 0.013 per cent. sulphur, which is
what the writer also obtains in these steels by that method.
At these works the malleable iron used for making crucible
steel is bought under a guarantee not to exceed 0.016 per cent. in
sulphur.   An accurate method of determination is plainly to be
desired.

From the above table it seems that sometimes the evolution
method is accurate and sometimes not; it is impossible, therefore,
to find a correction that will be a true one in all cases and the
practice common in western Pennsylvania of standardizing the
iodine solution against a standard steel of the same kind as those
to be worked on must also fail at times, although it is perhaps
not unlikely that the error is more regular and constant with
steels than with irons.   The best that can be done seems to be to
note the greatest error in a series of tests and use one-half this
error as a correction.   According to this plan the writer, when
using this method, increases his results one-fourth ; thus, for
instance, 0.2 per cent. is called 0.025 per cent., and 0.012 per
cent. is made 0.015 per cent.   This, of course, is far from satis-
factory, but seems to be the best that can be done with the
method.

A difficulty in the aqua regia method is the contamination of
the barium sulphate with iron oxide when the precipitation is
made in solution not containing much free acid.   Professor J. O.
Arnold (steel works analysis) meets this difficulty by making the
precipitation in the cold, but a precipitation made by the writer
in this way gave a very low result, showing that precipitation
in this manner cannot always be relied on as complete.   Precipi-
tating as directed by Blair, but with 5 cc. only of strong hydro-
chloric acid present in the liquid while preventing ferric oxide
contamination, brought results 0.004 to 0.008 per cent. (generally
the latter) too low, but it was found by many experiments that
with this amount of acid (5 cc.) present, and with one-half hour's
boiling (and standing over night), the precipitation is at least as
nearly complete as by the Blair procedure and no ferric oxide con-
tamination ever occurs, although in both methods the precipita-
tion is rarely absolutely complete as may be found by evaporating

the filtrate to first appearance of a scum, taking up with a little hydrochloric acid and water and filtering, carrying the blank, or dummy, test to the same length. Sixty-two tests (5 cc. free acid, one-half hour's boiling) showed as follows :

Number of tests in which precipitation was complete.... 9
" " " " " 0.001 to 0.002 per cent. was found in filtrate 34
" " " " " 0.003 to 0.004 " " " " " 11
" " " " " 0.005 to 0.008 " " " " " 8

In these losses are included also the barium sulphate dissolved by the hydrochloric acid wash used to free the precipitate from iron.

In these tests the sulphur percentage ranged from 0.015 to 0.09 per cent. The amount of sulphur unprecipitated does not depend upon the total amount—may be little in high sulphur steels and *vice versa*. So it is advisable in all cases to make a plus correction in the result of at least 0.002 per cent.

In Blair's " Chemical Analysis of Iron " the warning is given that the use of aqua regia in dissolving the drillings seems to result in loss of sulphur. Nevertheless it is necessary to use some little hydrochloric acid in the case of high carbon steels toward the end to effect complete solution. The following results obtained in the regular course of work were suspected of being low and the determinations were repeated, using the hydrochloric acid more sparingly :

No.	First determination. Percentage of sulphur.	Repeated, using HCl more sparingly. Percentage of sulphur.
609	0.005	0.013
611	0.004	0.011
814	0.014	0.020

LABORATORY OF HENRY DISSTON & SONS' STEEL WORKS,
PHILADELPHIA, PA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 55.]

ALLOYS MADE IN THE ELECTRIC FURNACE.

BY LEWIS P. HAMILTON AND EDGAR F. SMITH.

DURING the past year various alloys were made by us. We desire here to give a sketch of the furnace in which they were produced, and also to briefly describe the products, as they possess interest and perhaps value.

15-23

THE FURNACE.

The + carbon a is of convenient length and 2 cm. in diameter ; the — carbon b is 1.5 cm. in diameter, while c represents a No. 1 Dixon graphite crucible, which has an interior width of 5 cm. and a depth of 7 cm.   It was placed in d, a second graphite crucible, 1 decimeter across the top.   The space, e, between the
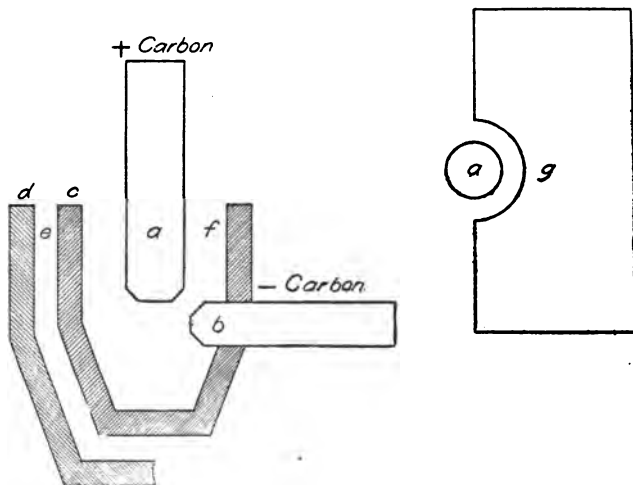
two crucibles, was filled with magnesia. g is one of two carbon plates, 1.5 cm. in thickness, which served as a cover.

It is absolutely necessary that the carbon, b, should make a good contact with the crucible, c, to avoid the formation of an arc at their juncture which would destroy the crucible.   The carbon is inserted in the crucible at about 3 cm. from the bottom.   To obtain products free from carbon, c is lined with magnesia.

OPERATION.

The material to be melted was introduced into the crucible until it was about even with the carbon, b, and then the arc was started between the two poles by means of a thin pencil of carbon.   The crucible was next covered in part by g and the remainder of the material was introduced from time to time until 150 to 200 grams had been added.   The cover, g, was then adjusted and the current allowed to run for a while longer.   The full period of action was usually ten to fifteen minutes.

The current used in the fusions equaled from 145 to 165 amperes, and from 25 to 70 volts, although the average voltage was 35.

ALLOYS.

1. This first alloy contained copper, tungsten, iron, and gangue. It was made by fusing together commercial copper and a tungsten matte which had been previously obtained by reducing the mineral wolframite in the furnace with carbon. It was lighter in color but very much harder than ordinary copper ; indeed, it proved to be the hardest of the copper alloys. Its specific gravity was found to be 7.98. Its analysis showed 66.88 per cent. of copper, 23.03 per cent. of tungsten, 5.74 per cent. of iron, and 5.04 per cent. of gangue.

2. A matte of titanium was first prepared by reducing 100 grams of rutile with 15 grams of carbon and fusing the product with copper. The alloy had a brass-like appearance ; it was tough but not so hard as the preceding product, and its specific gravity equaled 7.616. It gave, upon analysis, 90.98 per cent. of copper, 3.12 per cent. of titanium, 3.51 per cent. of silicon, and 2.08 per cent. of carbon.

3. The mineral columbite was reduced with carbon in the furnace, and the resulting matte then fused with metallic copper. The product did not differ in appearance very much from metallic copper. Its specific gravity was 8.38.

ANALYSIS.

	Per cent.
Copper	95.01
$Cb_2O_5 + Ta_2O_5$	2.01
Gangue	2.57
	99.59

4. Metallic copper and a molybdenum matte were fused together. The alloy, grayish red in color, was much harder than copper, but not so hard as the alloy of copper and tungsten. Its specific gravity was 7.934.

ANALYSIS.

	Per cent.
Copper	78.53
Molybdenum	8.53
Iron	2.71
Carbon	2.42
Gangue	8.02
	100.21

5. Chromium oxide and metallic copper were fused in a carbon crucible. The product was gray-red in color, and in hardness stood next to the alloys containing tungsten and molybdenum. Its specific gravity equaled 8.3146.

ANALYSIS.

	Per cent.
Copper	88.18
Chromium	3.22
Iron	1.35
Carbon	2.38
Gangue	4.13
	99.26

6. A tungsten matte was fused down with equal parts of metallic copper and aluminum, giving an alloy yellow in color, which showed the following composition :

ANALYSIS.

	Per cent.
Copper	34.11
Aluminum	24.89
Tungsten	32.67
Iron	2.12
Gangue	6.56
	100.35

7. Ten grams of metallic iron, 10 grams of titanium matte, and 10 grams of commercial metallic tungsten were fused together. Six to 8 grams of ferric oxide were added during the fusion. The product was steel-gray in color, of specific gravity 6.707, and gave the following :

ANALYSIS.

	Per cent.
Iron	82.15
Titanium	7.28
Tungsten	1.66
Gangue	6.63
Carbon	2.30
	100.02

8. An alloy of iron, chromium, and titanium was made precisely like the preceding example. It was steel-gray in color with a very distinct fracture, and the specific gravity 6.464.

ANALYSIS.

	Per cent.
Iron	76.41
Chromium	16.29
Titanium	2.47
Silicon	2.39
Carbon	3.14
	100.70

By greatly increasing the quantity of chromium in the fusion a product was obtained which had the following composition :

ANALYSIS.

	Per cent.
Iron	53.03
Chromium	40.37
Titanium	2.65
Gangue	4.33
	100.38

9. The matte resulting from the reduction of 100 parts of columbite and 15 parts of carbon, in the electric furnace, was fused down with an excess of metallic iron. The product was brittle and steel-gray in color.

ANALYSIS.

	Per cent.
Columbium	59.76
Tantalum	18.77
Iron	15.73
Gangue	5.12
Tungsten	0.63
	100.01

10. A matte of columbium and tantalum, a matte of titanium from rutile, and an excess of metallic iron were fused in the furnace and yielded an extremely hard, gray-colored alloy, which analyzed as follows :

ANALYSIS.

	Per cent.
Iron	80.03
Columbium	10.15
Tantalum	2.91
Titanium	3.18
Carbon	1.99
Silicon	2.14
	100.40

A COMPARISON BETWEEN THE BROMINE AND IODINE ABSORPTION FIGURES OF VARIOUS OILS.

BY H. T. VULTÉ AND LILY LOGAN.

A N examination of the existing tables for the bromine and iodine figures for the various oils discloses so many inconsistencies and obvious inaccuracies that the need for a revision of these tables is apparent. Such a revision is offered as the result of the present investigation. The work has been very carefully carried out in accordance with the methods described below, and the figures given are the results of so many repetitions that there is comparatively little opportunity for error.

In regard to the comparative accuracy of the two figures, the bromine absorption figure presents some decided advantages. Errors in the determination of this are largely due to faulty manipulation, while the iodine absorption is affected by many outside circumstances, such as change in temperature, during the much longer time required for the operation. Furthermore, in the case of bromine, loss from substitution can be readily determined by the use of potassium iodate, while, in the case of iodine, this test is of comparatively little value. On the other hand, substitution is much more likely to occur in the case of bromine, which offsets, to a great degree, the objections to the use of iodine named above.

The details of the methods employed in the present investigation are as follows :

1. Iodine Absorption Figure.—A solution of mercury bichloride and one of iodine were made up according to the original method of Baron Hübl, that is, with at least one molecule of $HgCl_2$ to every 2 atoms of iodine. A solution of o.10 normal sodium hyposulphite was then prepared and standardized by means of potassium bichromate. Equal parts of the first two solutions were mixed together and allowed to stand for twelve hours in the dark before use. Thin Erlenmeyer flasks, having ground-glass stoppers with gutter between flask and stopper, were used for this operation. A weighed portion of the oil was dissolved in 10 cc. chloroform, 25 cc. of the previously prepared mixed Hübl solution added, the flask sealed by filling the gutter with a solution

of potassium iodide, and the whole set away in the dark for twenty-four hours. A blank was run in connection with each determination. A solution of potassium iodide was then added in sufficient quantity to prevent precipitation, and the contents of the two flasks titrated with the sodium hyposulphite solution. The flasks should be frequently shaken during the titration, in order that the layer of chloroform may be gradually deprived of color, and a sharp end reaction may be had. When the operation was nearly completed, a few drops of starch solution were added in order to obtain a sharper change in color. The starch solution should be added as late as possible in order to prevent carbonization.

2. *Bromine Absorption Figure.*—The determination of this figure was carried out almost exactly as proposed by Dr. McIlhiney[1] except that the wait before titration was increased to from twenty to thirty minutes. The end reaction is less sharp by this process than in the Hübl determination on account of a yellowish tinge in the liquid which masks, to some extent, the disappearance of the starch blue. It is to be noted also that, bromine being more unstable in character than iodine, decomposition of the addition-product more readily takes place and, therefore, a return of the blue color is more likely to follow decolorization. On this account the determination of the substitution-figure should be hastened as much as possible.

A table showing the results obtained with fifteen different oils, by the methods described above, follows. In this table the oils are given in the order of increasing divergence between the bromine and iodine figures. The oils examined are divided into five classes according to the characteristics which they present. The first class, comprising eight oils, shows so close an agreement between their bromine and iodine figures that it evidently makes but little difference in which way their addition-factor is determined. In fact, reasoning from analogy, we may assume that this is true of all vegetable oils of simple constitution, together with whale and lard oils.

Sperm oil, being a wax, is placed in a class by itself and, as might perhaps be expected, gives somewhat erratic figures.

The class comprising rape and castor oils presents marked char-

[1] This Journal, 21, 1084.

acteristics.   In the former oil, substitution seems to take place to a greater extent with iodine than with bromine; this is probably due to the greater length of time necessary to carry out the Hübl process.   Traces of sulphur in rape oil, acquired during the process of manufacture, may also exert some influence upon the action of iodine on this oil.   In the case of castor oil, the dihydroxy group may set up an oxidation which would account for the difference observed between the two values.

The complex structure of the three fish oils following, probably causes some absorption of bromine which is not direct substitution, but which accounts for the greater bromine figure observed.

	Iodine. -	Iodine calculated from bromine.	Difference of averages.	Difference of nearest figures.
I. Olive oil	79.70–80.40	80.31	0.26	0.09
Cottonseed oil .	97.50	97.41–97	0.295	0.09
Poppyseed oil .	127.98–128.55	128.37	0.055	0.28
Linseed oil	155.12–155.52	154.80	0.52	0.32
Sw't almond oil	90.53–89.64	90.20–89.64	1.08	0.33
Peanut oil.....	100.71–100.76	101.26	0.523	0.50
Whale oil ...	128.00	127.45–127.38	0.585	0.50
Lard oil	76.99–77.36	76.03–75.88	1.22	0.96
II. Sperm oil......	79.95–79.76	82.39–82.08	2.422	2.13
III. Rape oil.......	103.69–103.37	99.03–98.56	4.60	4.17
Castor oil	86.32–87.15	78.74–78.71	8.01	7.58
IV. Seal oil	93.31–93.99	103.09–103.74	9.765	9.10
Cod-liver oil...	122.09–122.79	132.86–132.18	10.08	9.39
Menhaden oil..	176.5–175.65	186.94–186.86	10.825	10.36
V. Resin oil......	59.67–58.95	10.60–10.26	48.845	48.35

Examination of numerous samples of many different oils would probably disclose some regularity of action, and might lead to the formulation of some rules and tests for the detection of oils, either in combination or separately, from the relation between their bromine and iodine figures.   For example, the presence of menhaden oil in linseed oil could be easily detected in this manner.

The following table gives the substitution figures of all those oils tabulated above which show themselves at all capable of forming substitution products.   It will be noticed that only six out of the fifteen oils figure in this table.

	Total bromine.	Addition figure.	Substitution figure
Cod-liver oil........	85.16–84.67	84.52–84.09	0.63–0.58
Average........	84.91	84.305	0.605
Menhaden oil.......	120.10–120.30	118.88–118.93	1.22–1.27
Average........	120.15	118.905	1.245
Sweet almond oil....	59.54–59.15	57.38–57.02	2.16–2.13
Average........	59.345	57.20	2.145
Sperm oil	54.61–54.56	52.41–52.21	2.20–2.34
Average........	54.585	52.31	2.27
Castor oil	52.62–52.80	50.09–50.07	2.53–2.73
Average..... ..	52.71	50.08	2.63
Resin oil..........	108.67–109.23	6.74–6.47	101.93–102.76
Average........	108.90	6.605	102.345

As will be seen upon examination, the foregoing table gives results differing widely from those of other experimenters. In cases where the substitution is small this is probably due, in part at least, to experimental error, as great care is necessary in the conduct of the operation. Errors are titrated for, along with substitution, and the result obtained is compounded of these two items. In connection with this investigation, the recent article of Marshall[1] on the " Iodine Value of Oils" should also be noted.

Attention should also be called to the fact that several of the oils examined above were somewhat rancid and it is probably due to this fact that sweet almond oil shows substitution.

THE USE OF METALLIC SODIUM IN BLOWPIPE ANALYSIS.

BY CHARLES LATHROP PARSONS.

THE use of sodium carbonate to assist the action of the reducing flame has long been customary in blowpipe analysis, and is adopted by all text-books on the subject. The reducing action is partly due to the formation of sodium cyanide but more largely to the formation of gaseous sodium and carbon monoxide. At best its action is slow and nothing more severely tests the skill of the beginner than the attempt to obtain a button of metallic tin from cassiterite, or the sulphur reaction from gypsum. In general it is much more difficult to reduce an oxide or sulphide before the blowpipe, than it is to cause the opposite reaction to take place by means of the oxidizing flame.

[1] *J. Soc. Chem. Ind.*, (1900), p. 213.

Therefore, if the assay is not kept in the reducing zone of the flame a reoxidation will almost certainly take place.

The great reducing power of powdered aluminum has been well illustrated by Goldschmidt and Vautin,[1] and, although the fact that this property is possessed also by magnesium and sodium has long been known, W. Hempel[2] seems to have been the first to propose the use of the latter as a reagent in qualitative analysis. Hempel calls attention to the ease with which reduction may be brought about by sodium, but states that it does not give satisfactory results on charcoal. He recommends that the sodium be flattened out upon an ordinary filter-paper, and after being mixed with the powdered substance folded once and then rolled so that a double layer of paper is between each layer of sodium. This roll is next enclosed in a spiral of iron wire, set on fire in a Bunsen flame and cooled in the unburned gas below. It is next triturated with water in an agate mortar, and the residue carefully examined.

I have found these details to be quite unnecessary and that the reaction takes place with the greatest ease upon charcoal. To the operator who has been used to the much more tedious reduction with sodium carbonate the quickness and certainty of the results are almost startling, and the reduction takes place with silicates, chlorides, carbonates, borates, sulphates, sulphides, etc., with as much ease and accuracy as with the oxides themselves. The method is extremely simple.

A small piece of metallic sodium, not more than 3 or 4 mm. in diameter, is hammered out flat on some smooth surface. The substance to be reduced is powdered and spread upon it, pressed into the metal with the hammer and the whole turned and kneeded into a little ball with a knife blade. It is then placed upon a slight depression in a piece of charcoal and ignited with a match or the Bunsen flame. A momentary flash ensues, and the reduction is accomplished. The residue is now heated before the blowpipe, and as the sodium oxide and hydroxide immediately sink into the charcoal, any fusible metallic particles collect easily into a button and may be recognized in the usual manner. Volatile metals, like zinc, oxidize and yield with surprising· readiness their characteristic coatings and on digging up

[1] *J. Soc. Chem. Ind.*, **17**, 545.
[2] *Ztschr. anorg. Chem.*, **16**, 22.

a little of the charcoal, moistening with water and placing upon a silver coin, the "Hepar" reaction is obtained if sulphur was present in any form.   It is perhaps superfluous to add that this last reaction is certain in its conclusions only when carried out upon a piece of charcoal uncontaminated by previous tests.

Applied to minerals the method yields results, but little less certain than when pure salts or oxides are reduced.   Galenite yields at once a button of lead which in the oxidizing flame gives the lead coating without a trace of the white coating of sulphate which ordinarily results.   Garnierite gives a residue of silicon and magnetic nickel to which the bead test can be immediately applied. Chrysocolla and cassiterite yield buttons of copper and tin respectively as readily as a button of lead is obtained from cerusite.   Even chromite is immediately reduced, and if the residue is powdered the iron may be quite largely separated from the chromium by means of the magnet.   Barite, celestite, and gypsum show with ease the sulphur reaction and the residue if moistened with hydrochloric acid gives the flame tests far more rapidly than if applied to the powdered minerals.   In general the method is applicable whenever reduction can take place and whenever the reduced material yields characteristic reactions more readily than the mineral itself.

The metallic sodium does not need to be kept under naphtha but may be supplied to a class in small rubber-stoppered widemouthed bottles.   A lump of sodium two or three centimeters in diameter will keep for months in this manner with only superficial oxidation.   It must, of course, be carefully kept away from water or moisture.   In rolling up the sodium and substance to be reduced into a ball, the metal should not be touched with the fingers for with one or two of the more easily reduced oxides or sulphides, the reaction sometimes begins spontaneously.   This takes place quite readily with the peroxide of lead.   Large quantities of sodium should be avoided or the reaction may become dangerously violent.

From my experience in its use with classes during the last two years, I feel sure that sodium will soon be universally employed as a reagent in blowpipe laboratories.

ON HEPTANE FROM CONIFEROUS TREES.

By W. C. BLASDALE.

IN 1879, Thorpe[1] showed that the liquid at that time sold in San Francisco under the name of abietene, and there largely used as a cleansing agent and insecticide, consisted of nearly pure, normal heptane. This substance had been previously examined by Wenzell[2], and was by him reported to be obtained by distilling the exudation of *Pinus Sabiniana*. At the present time this substance is not on the market, though certain abietene cough-remedies find a limited sale. These latter preparations were shown by Lemmon[3] to be derived from *Pinus Jeffreyi*.

The occurrence of a normal hydrocarbon of the paraffin series as a vegetable product is of unusual interest and should be fully confirmed. The above facts would seem to warrant a reexamination of the exudations of the species named, as well as those of the other numerous Pacific Coast conifers. The difficulty of obtaining material in sufficient quantity and of unquestioned authenticity for such an investigation is a serious one, as many of the species yield only small amounts of such exudations, and many are difficult of access. The author has been able at various times to collect small samples of such material, representing five different species, and has made such examination of these as the nature of the material would permit. The samples are described as follows :

1. *Pinus Jeffreyi.*—Collected at Lake Tahoe from stumps of recently cut trees. The fresh material consists of a clear, white liquid of about the consistency of glycerine, and has a pleasant aurantiaceous odor ; on standing, it rapidly thickens, loses its pleasant odor and eventually forms a hard, yellow colophony. On distillation with steam the sample yielded about three per cent. of a mobile colorless liquid. This distillate was purified by treatment with concentrated sulphuric acid, washed with water, dehydrated with calcium chloride and redistilled. The greater portion distilled over between 96° and 98°, but some portions boiled as high as 112°.

[1] *J. Chem. Soc.*, 35, 297 ; *Am. Chem. J.*, 1, 155.
[2] *Am. J. Pharm.*, 4th series, 2, 97.
[3] *San Francisco and Pacific Druggist*, 1, 17.

2. *Pinus Sabiniana.*—Collected at the Hoopa Valley from incisions made in the trunks of the trees. The secretion closely resembles that of *P. Jeffreyi* but is more viscous. It yielded about 10 per cent. of a mobile distillate which was purified as that obtained from the previous sample.

3. *Pinus Sabiniana.*—A sample of the hardened resin naturally secreted from the trunk and branches. It was collected in Lake County by Mr. W. H. Rees, and was treated the same as the previous samples.

4. *Pinus Murryana.*—Collected at Lake Tahoe from recently peeled, but still living, trees. It was of a light yellow color, a semisolid consistency, and had a pronounced turpentine odor. On distillation it yielded a liquid of pronounced terpene odor, most of which distilled over between 153° and 160°, but portions of it boiled as high as 180°. The former fraction was redistilled and the portion boiling between 158° and 160° used for the determinations enumerated below.

5. *Abies Concolor var. Lowiana.*—Obtained at Lake Tahoe from the cavities in the outer bark. It is a light yellow oleo-resin which closely resembles Canada balsam (from *Abies Canadensis*) and could undoubtedly be used as the equivalent of it. It yielded 20 per cent. of a terpene-like liquid, most of which distilled between 155° and 160°.

6. *Pseudotsuga Taxifolia.*—The hardened natural exudation collected in Mendocino Co. On distillation, it yielded about 9 per cent. of a terpene-like liquid. On redistilling, the larger part passed over between 157° and 160° the remainder between 160° and 165°.

In the following table are tabulated the results obtained from an examination of the distillates referred to above. Corrections for varying barometric pressure, etc., have not been applied since the small amounts of liquid obtained (from 8 to 20 cm.) did not permit of a satisfactory purification of the samples. A comparison of the figures there reported with the numbers representing the normal constants of heptane on the one hand, and of the various terpenes on the other, gives sufficient evidence of the fact that both *P. Jeffryi* and *P. Sabiniana* yield normal heptane, while the other species mentioned yield terpenes

similar to those obtained from other coniferous trees.   The exact
character of the terpenes present can not be determined from the
data presented.

Sample No.	Boiling-point.	Sp. gr. at 15°	Index of reaction at 15°	Specific rotation.	Vapor-density.	Iodine absorption.
1	96°–97°	0.6863	1.3905	0	..	0
2	96°–97°	0.6840	1.3887	+2′	..	0
3	97°	0.6860	1.3902	+3′	3.54	0
4	158°–160°	0.8640	1.4765	−15° 23′	..	high
5	155°–160°	0.8578	1.4738	− 7° 9′	..	very high
6	157°–160°	0.8583	1.4754	−41° 12′	..	high

CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA,
January 11, 1901.

ON THE HEAT OF COMBUSTION AS A FACTOR IN THE ANALYTICAL EXAMINATION OF OILS; AND THE HEATS OF COMBUSTION OF SOME COMMERCIAL OILS.[1]

BY H. C. SHERMAN AND J. F. SNELL.

INTRODUCTION.

THE accuracy, the rapidity of manipulation, and the moderate cost of the bomb calorimeters now in use, have made it practicable for chemists to employ the determination of heat of combustion (or calorific power) not only for the valuation of fuels, but as an aid to, or check upon, the chemical analysis of other organic materials.   The comparison of the values actually determined by the calorimeter with those calculated for the constituents found by analysis has been used for some years as a check upon the accuracy of the analyses of foods and physiological products, especially by Atwater and his associates at Middletown, Conn., and by Wiley and Bigelow in the U. S. Department of Agriculture.

It is evident that this method of checking the results of proximate analysis can be applied in any case in which the calorific values of the determined constituents are accurately known. The determination of heat of combustion may also give direct

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[1] A considerable part of the work here recorded was carried out in the laboratories of Wesleyan University for the privileges of which, as well as for the use of the bomb calorimeter employed, we are greatly indebted to Prof. W. O. Atwater.

aid in distinguishing between similar materials. Butter, having a relatively high proportion of fatty acids of low molecular weight, has a lower heat of combustion than lard or margarine and this fact has been utilized by de Schweinitz and Emory in testing the purity of butterfat.[1] This principle would evidently find little application among the fatty oils since they show little variation as regards the mean molecular weights of the fatty acids present. Neither is the heat of combustion greatly affected by the presence of unsaturated acids. Stohmann (using the chlorate method) found only a small difference between stearic and oleic acids and almost no difference between olive oil and linseed oil.

However, it seemed likely, that, on the one hand, oils rich in hydroxy-acids like castor oil, and on the other hand, waxes like sperm oil or non-fatty oils like resin and petroleum oils, might differ sufficiently from the ordinary fatty oils to give some value to the determination of heat of combustion as one means of detecting mixtures of oils of these different classes.

It occurred to us, moreover, that the oxidation which takes place when an oil "dries" must result in a loss of calorific power and that a measure of this loss might often be of more value than the simple determination of increase in weight. A lubricant consisting of a mixture of semidrying fatty oil with petroleum might show little or no change in weight on heating in contact with the air, the oxidation of the former oil being obscured by the partial volatilization of the latter. Since, however, the volatilization of hydrocarbons by decreasing the amount of combustible matter would increase the loss of calorific power (calculated upon the original weight) it is probable that this determination would immediately indicate the objectionable nature of such a sample. Even in the absence of hydrocarbon oils, the information obtained by determining the loss of calorific power on exposure may sometimes be of value in judging the quality either of an oil intended to "dry" or of a lubricant in which any such tendency is highly objectionable.

In some drying experiments already made, in which oils were exposed at about 50° for forty hours, we have found a loss of calorific power amounting to over ten per cent. in the case of

[1] This Journal, 18, 174.

linseed oil, while lard oil subjected to the same treatment lost less than one per cent. The results, are, however, considerably affected by variations in the temperature employed and in the amount of surface over which the oil is spread. These conditions are still under investigation and the discussion of this subject will be left for a later paper.

We give below the heats of combustion of several samples of commercial oils with some consideration of the relation of this value to the analytical constants most commonly determined.

THE HEATS OF COMBUSTION OF SOME COMMERCIAL OILS.

With the exception of mineral oils intended for fuel,[1] few combustions of oils appear to have been recorded. Berthelot[2] quotes only the results obtained by Stohmann ;[3] *viz.*, two samples of linseed oil, 9488 and 9439 calories per gram; two of poppyseed oil, 9597 and 9562; two of rapeseed oil, 9627 and 9759; and three of olive, 9467, 9458, and 9608. The determinations were made by the chlorate method and afterward corrected by dividing by the empirical factor 0.9857, which was derived from a comparison of the results obtained on solid animal fats by the two methods. Gibson,[4] who also used the chlorate method, found for olive oil 9471, and for sperm oil, 10001 calories per gram. Wiley and Bigelow,[5] while studying the calories of combustion of the constituents of cereals, made the following determinations upon oils extracted and purified in the laboratory: wheat oil, 9359; rye oil, 9322; maize oil, 9280 calories per gram. Merrill[6] found the heat of combustion of a sample of cocoanut oil pressed in the laboratory to be 9066 calories per gram.

In addition to these oils a considerable number of "ether extracts" have been examined by Stohmann,[7] Wiley and Bigelow,[8] Atwater and associates (unpublished) and by Merrill.[9] The

[1] Poole, "Calorific Power of Fuels" (1898), pp. 238-240, quotes determinations of heat of combustion of several samples of mineral oils by various observers but without sufficient detail as to the methods by which they were obtained to enable us to compare them with those here recorded.

[2] "Thermochimie," Tome II, p. 565.

[3] See review article in Experiment Station Record, VI, 601.

[4] Report of the Storrs (Conn.) Experiment Station for 1890, p. 190.

[5] This Journal, 20, 309.

[6] Bull. 65, Maine Experiment Station, p. 111.

[7] *Loc. cit.*

[8] *Loc. cit.*

[9] *Loc. cit.*

latter's work upon the oils extracted from nuts included the determination of the more important "constants" and these would indicate that the samples examined did not differ greatly from the corresponding oils obtained by commercial methods.

As a rule the heats of combustion of ether extracts have been found distinctly lower than those of the corresponding commercial oils, the difference being doubtless due to the presence of other ether-soluble substances.

Our own work has been done entirely upon commercial oils, some of the samples being fresh and presumably typical, while others are known to be more or less altered by age and exposure.

Apparatus and Methods Employed.—The heats of combustion were determined with a bomb-calorimeter of the Atwater-Blakeslee type.[1] Accordant results for the hydrothermal equivalent of the apparatus were obtained (1) by calculation from the weights and specific heats of the component materials ; (2) by five combustions of cane-sugar, the quantity of heat liberated by the combustion being assumed to be 3959 calories per gram of substance burned ;[2] (3) by three combustions of benzoic acid, the heat liberated being assumed to be 6322 calories per gram.[3]

The heats of combustion given in the table are the mean of. two (or in some cases three or four) determinations. The average deviation of individual determinations from the mean was ± 0.12 per cent. of the value found (about 11 calories). In only three cases did the deviations exceed ± 0.25 per. cent.; *viz.*, linseed oil III (No. 3), + 0.39 and — 0.31 per cent., petroleum III (No. 40) ± 0.38 per cent., and rape oil II (No. 18) ± 0.30 per cent.

The results obtained with the bomb-calorimeter are, of course, heats of combustion at constant volume. To reduce these to heats of combustion at constant pressure ·it is necessary in the case of solid or liquid compounds containing only carbon, hydrogen, and oxygen to add

$$(\tfrac{1}{2} p - q) \frac{T}{M} \text{ calories per gram,}$$

[1] W. O. Atwater and O. S. Blakeslee: "Improved Forms of Bomb-Calorimeter and Accessory Apparatus," Storrs (Conn.) Experiment Station Report for 1897, p. 199.

[2] Average of the results of Berthelot and Vieille (three determinations): *Ann. chim. phys.*, [6], 10, 458 (1887); Stohmann and Langbein (four determinations): *J. prakt. Chem.*, [2], 45, 313 (1892); and Atwater and Tower (seven determinations): Unpublished.

[3] Identical average of the results of Longuinine (four determinations): *Ann. chim. phys.*, [6], 13, 330 (1888); and of those of Stohmann, Kleber, and Langbein (four determinations): *J. prakt. Chem.*, [2], 40, 128 (1889).

p being the number of atoms of hydrogen and q the number of atoms of oxygen in the molecule, M the molecular weight of the substance and T the absolute temperature of the calorimeter. The correcting terms for the principal constituents of oils at 20° C. were calculated from the elementary composition and from the results thus found we have estimated the following corrections for the oils included in this investigation: American petroleums, 22 calories; sperm oil, 18 calories; castor oil and rosin oil, 14 calories; all oils consisting essentially of glycerides of non-hydroxylated fatty acids, 15 calories.

Method of Kindling the Samples.—The device employed to insure the ignition of the oil in the bomb is one which we have not seen described. The oil was absorbed upon a small amount of fibrous asbestos, such as is used in Gooch crucibles, contained in the small platinum capsule ordinarily used in combustions of solids, and was ignited directly by the electrically fused iron wire. This method has proved perfectly satisfactory and is obviously more accurate than that of burning, with the oil, a quantity of kindling substance—such as a block of cellulose or a gelatine capsule.

Determination of "Constants."—The usual methods were followed. The specific gravity was determined by means of a carefully calibrated Westphal balance. Free acid was dissolved by vigorous shaking with alcohol, titrated with tenth-normal alkali and calculated as oleic. For the determination of the iodine absorption, the solutions of iodine and of mercuric chloride were prepared separately and mixed only about twenty-four hours before use. The flasks used were similar to those described by Vulté and Gibson.[1] About twice as much iodine was added as was expected to be absorbed and the whole allowed to stand in a dark closet at room temperature for eighteen to twenty hours. The determinations were usually made in sets of six to twelve, several "blanks" being run with each set.

Description of Samples Examined.—1. Linseed oil from seed grown in Dakota. Prepared by crushing the seeds between rollers and pressing in hydraulic presses. This sample was obtained directly from the manufacturers, and from the description given by them it must have been less than six months old when examined.

[1] This Journal, 22, 457.

2. Linseed oil purchased in open market. Origin unknown. Had been kept about two years in a dark closet in the laboratory.

3. Linseed oil several years old. This sample had been kept for a long time in a bottle only partly filled, and had frequently been opened and exposed to diffused sunlight.

4. Boiled linseed oil of unknown history.

5. Poppyseed oil. This sample was several years old, but had been fairly well protected from light and air.

6. Maize oil furnished by the Glucose Sugar Refining Company. This sample came directly from the factory with the statement that it had been pressed from cooked corn germs, and had gone through no refining process, except that it was allowed to settle in a large tank before shipment. It was examined soon after being received.

7. Maize oil purchased in open market and kept in a closed can for about three years.

8. Crude maize oil of unknown history.

9. Prime summer-yellow cottonseed oil.

10. Choice summer-yellow cottonseed oil.

11. Choice summer-white cottonseed oil.

Nos. 9, 10, and 11 were kindly furnished by the Southern Cotton Oil Company through the courtesy of their chemist, Mr. Geo. F. Tennille, to whom we are also indebted for the following statement : "These oils are of undoubted origin, and were refined to a yellow by caustic soda only. The white oil was made from a choice yellow by bleaching with fuller's earth and then deodorizing by a secret process."

12 and 13. Samples of crude cottonseed oil of unknown history.

14. Cottonseed oil which had been kept in a partly filled bottle for some time.

15. Very old sample of winter-yellow cottonseed oil, showing in marked degree the effects of oxidation, although, as its history is unknown, it may have been abnormal when fresh.

16. Commercial sesame oil, about one year old.

17. Commercial rape oil examined as soon as received.

18 and 19. Commercial rape oils which had been in the laboratory for some years.

20. Castor oil purchased from retail druggist.

21. Castor oil of unknown origin, at least a year old.

22. Commercial peanut (arachis) oil, about a year old.

23. Commercial almond oil, about a year old.

24. Commercial almond oil, several years old.

25. " Best " commercial olive oil, about a year old.

26. Olive oil of unknown origin, labeled " special."

27. Refined menhaden oil. This sample was several years old but had been kept air-tight in a full bottle.

28. Crude commercial menhaden oil, about a year old.

29. Fresh " Bergen " cod-liver oil.

30. Old sample of cod-liver oil; discolored; origin unknown.

31. Whale oil believed to be entirely pure. The sample was at least twenty years old but had been kept well corked in a full bottle.

32. Best commercial lard oil furnished us by Dr. A. G. Manns, chemist for Armour & Co. This sample was examined a few weeks after being received.

33. Lard oil " for lubricating," about a year old.

34. Commercial lard oil, four or five years old.

35. " Extra winter " lard oil which had been kept in a partly filled can for about three years.

36. Sperm oil obtained direct from makers. The sample was about ten years old but had been kept during most of the time in a well-stoppered bottle in a dark closet.

37. A rather heavy rosin oil of unknown history.

38, 39, and 40. Commercial petroleum oils intended for lubricating.

No.	Description of oil.	Specific gravity 15.5/15.5	Iodine absorption. Per cent.	Free acid as oleic. Per cent.	Heat of combustion per gram. Constant volume. Calories.	Heat of combustion per gram. Constant pressure. Calories.
1.	Raw linseed, I—1900; fresh···	0.934	182.4	4.30	9364	9379
2.	Raw linseed, II—1898········	0.938	175.9	1.22	9379	9394
3.	Raw linseed, III—old········	0.947	156.7	5.30	9215	9230
4.	Boiled linseed···············	0.953	150.7	7.40	8810	8824
5.	Poppyseed····················	0.926	129.6	2.66	9382	9397
6.	Maize oil, I—1900············	0.924	120.3	3.32	9413	9428
7.	Maize oil, II—1898···········	0.926	120.7	2.56	9436	9451
8.	Maize oil, III—crude·········	0.926	122.4	1.68	9419	9434
9.	Cottonseed, I—prime yellow··	0.920	102.5	0.20	9396	9411
10.	Cottonseed, II—choice yellow	0.921	106.4	0.32	9401	9416
11.	Cottonseed, III—choice white	0.923	105.5	0.08	9390	9405
12.	Cottonseed, IV —crude ······	0.927	103.2	2.28	9397	9412

No.	Description of oil.	Specific gravity 15.5 / 15.5	Iodine absorption. Per cent.	Free acid as oleic. Per cent.	Heat of combustion per gram.	
					Constant volume. Calories.	Constant pressure. Calories.
13.	Cottonseed, V—crude········	0.927	···	···	9336	9351
14.	Cottonseed, VI—rather old····	0.929	100.1	0.92	9323	9338
15.	Cottonseed, VII—old·········	0.941	93.7	2.03	9168	9183
16.	Sesame······················	0.924	105.3	1.65	9395	9410
17.	Rapeseed, I·················	0.922	107.4	0.82	9489	9504
18.	Rapeseed, II················	0.920	108.6	0.68	9462	9477
19.	Rapeseed, III···············	0.926	99.3	2.94	9412	9427
20.	Castor, I······· ···········	0.967	84.1	0.26	8863	8877
21.	Castor, II··················	0.964	86.9	2.18	8835	8849
22.	Peanut (arachis) ············	0.917	105.9	0.16	9412	9427
23.	Almond, I··················	0.919	98.1	5.13	9454	9469
24.	Almond, II·················	0.931	89.8	7.00	9311	9326
25.	Olive, I ····················	0.917	85.1	2.51	9457	9472
26.	Olive, II ···················	0.916	78.8	0.40	9451	9466
27.	Menhaden, refined···········	0.935	··	0.36	9360	9375
28.	Menhaden, crude············	0.934	··	1.92	9371	9386
29.	Cod-liver, fresh·············	0.927	165.6	0.56	9437	9452
30.	Cod-liver, old···············	0.938	137.3	1.50	9277	9292
31.	Whale ·····················	0.924	126.6	0.60	9473	9488
32.	Lard oil, I—1900············	0.917	74.3	0.74	9451	9466
33.	Lard oil, II—1899···········	0.919	72.5	1.25	9447	9462
34.	Lard oil, III············ ····	0.922	72.9	2.64	9394	9409
35.	Lard oil, IV ················	0.924	69.3	2.34	9372	9387
36.	Sperm oil········· ·········	0.886	78.7	0.78	9946	9964
37.	Rosin oil ···················	0.989	76.9	14.40	10145	10159
38.	Lubricating petroleum, I ·····	0.881	···	···	10797	10819
39.	Lubricating petroleum, II ····	0.897	···	···	10753	10775
40.	Lubricating petroleum, III ···	0.905	···	···	10682	10704

It will be seen that the sperm, rosin, and mineral oils are considerably higher in calorific value than the fatty oils and that among the latter the values are slightly higher for the non-drying than for the drying oils. Castor oil shows an exceptionally low value, due doubtless to the presence of ricinolein instead of olein as the principal constituent. Boiled linseed oil shows a similar low heat of combustion. The "choice summer-white" cottonseed oil does not seem to have been appreciably affected in iodine absorption or heat of combustion by the special refining process to which it has been subjected.

The samples which are known to be old and whose specific gravities are high and iodine figures low, have in all cases given

rather low heats of combustion. The variations of the latter value are evidently more closely related to those of specific gravity than to those of iodine absorption or acidity.

Oxidation induced by the action of light and air seems to have lowered the heat of combustion to almost the same extent that the specific gravity is raised, so that for oils of a given variety the product of these values is practically a constant unaffected by age and exposure. In the cases examined, this product is slightly higher for the drying than for the non-drying oils though the difference is necessarily less than that between the specific gravities. Among the ordinary fatty oils examined, the value of this product (large calories per gram $\times$ specific gravity at 15.5°) ranged from 8.80 in the case of raw linseed oil, II, to 8.63 in the case of the peanut oil. Castor and boiled linseed oils show somewhat lower values.

As compared with the ordinary fatty oils, this product is slightly higher for the sperm oil and considerably higher for the mineral and rosin oils.

By dividing the heat of combustion by the specific gravity, a value is obtained which ranges from 10.0 to 10.3 in the fresh fatty oils examined (though lower in case oxidation has taken place) and is considerably higher in sperm oil and mineral oils (in the cases examined 11.2 for sperm oil and 11.8 to 12.3 for the mineral oils).

Thus, it would appear that a determination of heat of combustion (which can be accomplished in forty to fifty minutes), especially when considered in relation to the specific gravity, may be of value in the detection of mineral or rosin oils in fatty oils, or of fatty oils in sperm oil.

Further experiments are now being made upon the relation of the specific gravity and heat of combustion with special reference to the effects of exposure to light and air. We hope to discuss later the more detailed applications of this method of studying the fixed oils, and, if possible, to extend it to the examination of essential oils.

QUANTITATIVE LABORATORY,
February, 1901.

THE QUANTITATIVE ESTIMATION OF HYDROGEN SULPHIDE IN ILLUMINATING GAS.

BY C. C. TUTWILER.

IN the manufacture of illuminating gas the importance of tracing the successive stages of purification of the crude gas from the time it leaves the retorts or water gas machine until it passes the purifiers is obvious, as by this means alone is it possible to determine the efficiency of the purifying plant and of the character of the raw material used, as well as the purity of the finished product. Tests on the purified gas are generally qualitative and are all that is necessary, as in most cities perfect freedom from obnoxious constituents is required by legislative enactment. This is particularly true of hydrogen sulphide on account of its exceedingly injurious products of combustion. The usual qualitative test for this impurity consists in allowing the gas to be tested, to impinge upon a piece of moist lead acetate paper for a few minutes, any discoloration showing the presence of hydrogen sulphide. It is, however, of great importance at times to know the exact hydrogen sulphide content of the unpurified or partly purified gas in order to ascertain the condition of the purifiers and the efficiency of the purifying material used. Where boxes are run in parallel it presents a ready means of ascertaining whether the work to be accomplished is equally distributed or is being done wholly or in part by one set of boxes. In order to ascertain this, it is necessary to make determinations at the inlet and outlet of the purifiers, and to be of value they must be made at practically the same time, hence the necessity for a rapid method of making the analysis.

The methods hitherto adopted in gas works have proved unsatisfactory on account of the slowness of the usual gravimetric estimations and the necessary manipulative skill required in making the determinations, besides a laboratory equipment not usually possessed by the smaller plants throughout the country. It was to overcome these difficulties that the apparatus about to be described was devised. Its action depends upon the

well-known reaction between hydrogen sulphide and iodine according to the equation

$$H_2S + I_2 = 2HI + S,$$

hydrogen iodide and free sulphur being formed. Although the suitableness of iodine for estimating hydrogen sulphide in illuminating gas was suggested by Bunte many years ago, it seems never to have come into general use, due possibly to the great care necessary to obtain accurate results with a Bunte burette. The
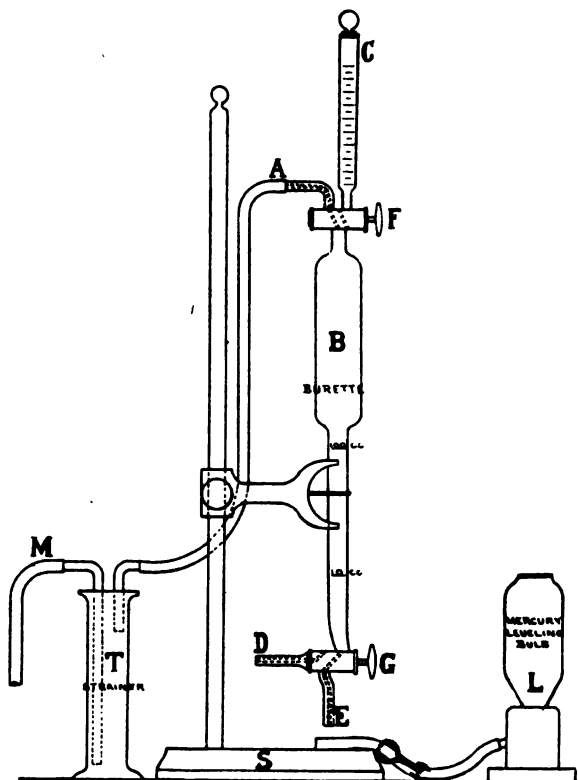
apparatus used in The United Gas Improvement Company's Works is shown in the accompanying sketch. It consists of a burette provided at top and bottom with three-way stop-cocks and communicating at the top through one of the outlets with a 10 cc. glass stoppered cylinder graduated into 0.1 cc. There are only two

graduations on the stem of the burette, one at the 100 cc. mark, the other, 50 mm. from the bottom stop-cock, dividing the remaining space into two divisions of about 5 and 10 cc. respectively. A mercury leveling bulb is attached to the lower stop-cock at E, and the burette mounted on a stand as indicated. When analyses are to be made on crude gas a tar-arrester consisting of a wash-bottle containing cotton is placed between the gas supply and the burette. The manner of using the burette is as follows :

Turn both stop-cocks so that A and E communicate with the interior of the burette. Connect gas supply to A, or to M, if testing crude gas, and let gas flow through the burette and out at E for a few minutes, thereby displacing the air by the gas to be tested for hydrogen sulphide. Close the bottom of the burette by turning G so that E communicates with D. Close F and disconnect from the gas supply at A. Allow the burette to stand for a few minutes until the gas reaches the temperature of the surrounding atmosphere, which should be noted. Attach leveling bulb tube to E and raise the mercury bulb until the mercury passes into the stop-cock, G, thus removing air from the rubber tube and E. Turn the cock so that E communicates with the interior of the burette, and bring the mercury up to the 100 cc. mark, thereby compressing the gas in the burette. Close the lower stop-cock and open B to A momentarily, in order to bring the gas in the burette to atmospheric pressure. Open B to E and draw the mercury back to G, closing the stop-cock by turning so that E communicates with D. We now have 100 cc. of gas measured at atmospheric temperature and pressure, under a negative pressure. Place the clip on the rubber tube and remove the same from E. Take the burette from the stand and by opening B to A allow the partial vacuum to draw into the burette about 5 cc. of starch solution from a portion contained in a small beaker. Close the cock and fill the graduate with a standard iodine solution, noting the reading. Admit the iodine solution into the burette, gradually shaking between each addition of three or four drops. Continue until the starch paste assumes a permanent blue color. Note the reading on the graduate which, subtracted from the previous reading, gives the amount of solution used. This, being multiplied by the number of grains 1 cc. iodine solution is equivalent to, gives directly grains H_2S per 100 cubic feet.

Suppose, therefore, that 5.2 cc. of iodine were required to give the blue color and 1 cc. = 100 grains, then the amount of hydrogen sulphide would be 5.2 × 100 = 520 grains per 100 cubic feet.

The strength of the iodine solution used is generally such that 1 cc. contains 0.0017076 gram of iodine per cubic centimeter. One cubic centimeter of this will then be equivalent to 100 grains H_2S per 100 cubic feet of gas.

Precautions.—The following precautions are necessary :

(1) For very accurate work, the starch solution should be previously treated with just enough iodine solution to color it faintly.

(2) The blue color must not be confused with the opalescent milky appearance given to the solution by the separation of free sulphur.

(3) For very accurate work, introduce correction for temperature and pressure, bringing the gas to 60° F. and thirty inches.

Extended use of the burette in our works has established its value beyond question as a quick and accurate substitute for the older methods. Very little skill is required in handling the apparatus, no more than can be acquired in a short time by any one of average intelligence. It will readily be seen that any variation in the strength of the iodine solution introduces no error in a determination of the percentage of impurity removed by a given purifier ; for example, if it was found that single tests of the gas, before and after leaving a purifier, showed 500 and 400 grains of hydrogen sulphide per 100 feet respectively, assuming that 1 cc. of the iodine solution is equivalent to 100 grains, then the efficiency of the purifier is 20 per cent.; that is, it is removing 20 per cent. of the total hydrogen sulphide impurity. If a subsequent examination of the iodine solution showed that 1 cc. was equivalent to 110 grains of H_2S, the calculations on this basis would still show that the purifier was taking out 20 per cent. of the hydrogen sulphide in the gas, for instead of there having been 500 grains in the inlet gas, there would actually have been 550, and the outlet gas would have had 440, 110 grains having been removed or 20 per cent. of total content as before. Errors of manipulation common to both determinations are also eliminated.

Note.—Since the above article was admitted for publication, a paper has been read by Mr. Carroll Miller, of Newark, before the New England Association of Gas Engineers,[1] giving in detail results of experiments on purification conducted with this apparatus. The employment of starch paste solution instead of mercury in taking the sample, is perhaps an advantage, as it is easier to handle and does away with the necessity in very exact work for drying out the burette after each determination. In using starch paste solution the burette is previously filled with the same, and the sample of gas taken by allowing the liquid to run out down to the 100 cc. mark, having previously purged the connecting hose with the gas to be analyzed. A question as to the accuracy of the apparatus brought from Mr. Miller the opinion that 15 grains of hydrogen sulphide per hundred feet of gas could escape detection. Before the apparatus was put on the market it was tested and found to be susceptible to as small a quantity as 3 grains per one hundred feet.

ON TRITOLYLCHLORMETHANE.

BY M. GOMBERG AND O. W. VORDISCH.

Received January 18 1901.

ONE of us[2] published recently a method for the preparation of triphenylchlormethane. We have tried the same reaction on toluene and find that the corresponding tritolyl compound can be obtained ·in this way. As the action of aluminum chloride upon a mixture of carbon tetrachloride and toluene was rather energetic we added, as is customary, a large excess of carbon disulphide in order to lower as much as possible the temperature of the reaction and to prevent the splitting off of the methyl groups. The yield of the tritolylchloride was in this way increased, but is still far from satisfactory. The compound was purified similarly to the triphenyl derivative. Sixty-two grams of carbon tetrachloride, 100 grams toluene, 150 cc. carbon disulphide, and 85 grams aluminum chloride, give about 22 grams of the chloride derivative, as we found from ten trials of this reaction.

	Calculated for $(C_6H_4CH_3)_3CCl$.	Found. I.	II.
Chlorine	11.08	9.93	10.85

[1] See *American Gas Light Journal*, **74**, No. 9, p. 325.
[2] This Journal, **22**, 752.

On boiling with alcohol the tritolylchlormethane gives the ethoxy compound, which can be easily purified by recrystalliza- tion from alcohol.   Melting-point, 105° C.

	Calculated for $(C_6H_4CH_3)_3C.OC_2H_5$.	Found.
Carbon	87.27	86.63
Hydrogen...............................	7.88	7.66

On boiling with water the carbinol is formed.   This work will be continued, and the action of metals upon the halogen com- pound will be studied.

UNIVERSITY OF MICHIGAN,
CHEMICAL LABORATORY,
    January 9, 1901.

REVIEW.   •

THE FOURTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.[1]

The grand amphitheater of the Sorbonne has seen many notable assemblages of scientific men, but probably the most distinguished body of chemists that its walls ever enclosed was that which met on the 23rd of July, 1900, to assist in the opening of the Fourth International Congress of Applied Chemistry.

This organization of chemists had its real origin during the World's Fair, when the chemists of the United States invited their professional brethren from all parts of the world to meet them in an international congress, which convened in Chicago, in 1893, under the auspices of the American Chemical Society, and the chemical section of the American Association for the Ad- vancement of Science.   In the address of welcome to this con- gress, I said :

"Chemistry is truly cosmopolitan.   There is no one country that can claim it entirely, either by birth or adoption, Wurtz to the contrary notwithstanding.   It is therefore entirely fit and proper that the chemists of all nations should now and then meet on common terms for the sake of mutually profiting by the advances and discoveries that each has made.   I believe that there will be brought before the present congress a proposal for the regular triennial meeting of the chemists of the world, after the plan which has been followed so successfully by our brethren, the geologists and physicians.   Were the object of such a con- gress only to listen to papers and addresses pertaining to the prog- ress and development of our science, it might well be asked

[1] Read before the Northeastern Section of the American Chemical Society, January 17, 1901.

whether such conventions are useful. The chemical journals of to-day fully cover the whole field of chemical activity, and thus even in the most remote mining camp the chemist and assayer may be fully *en rapport* with his fellows, the world over. But the objects of our congress are wider than the mere listening to papers. The chemist is a social being, and there is a life outside of the laboratory as beautiful and useful as the life within. The narrowness of an idea, and the flattening of isolation are to be avoided as the purpose of an investigation is to be pursued. The highest culture is not found in books, but in men. The power and splendor of a great and old university are not alone in its libraries and professors. There is a subtle influence of association that does more, often, than the lecture room to develop mind and mold character. And thus to widen his horizon and broaden his views the chemist must leave his desk and seek the acquaintance of his fellows. Every time you take a brother chemist by the hand you enlarge your life and extend your strength, and the farther apart the field of your activities, the greater the benefit.''

The congress of chemists at Chicago contained representatives from almost every civilized country, and the fruit of this conference, the first international conference of chemistry ever held, was manifested in the following year by a call issued for a congress of applied chemistry to meet at Brussels. The Brussels congress decided to hold the next meeting in Paris, and the Second International Congress of Applied Chemistry convened at the Sorbonne, the latter part of July, 1896. It was my good fortune to attend this meeting, as well as the meeting of the third congress which convened in Vienna, in July and August, 1898. Reports of the proceedings of both these congresses were published in the Journal of the American Chemical Society.

The Vienna congress decided to have its fourth meeting in Paris, in 1900, on account of the World's Fair which would be likely to bring together a larger number of representative chemists than could be collected in any other quarter at that time.

The functions attending the opening and closing of scientific congresses in Europe are somewhat more elaborate than we are accustomed to in democratic America. Evening dress and uniforms representing offices in civil life are not found in scientific functions in this country before 6 o'clock. Quite otherwise in Europe where the evening coat and the uniform of any learned body to which the member may belong are *en regle* even for morning functions.

The Fourth International Congress of Applied Chemistry was opened by Mr. Moissan, the president of the Committee of Organization. He said, in part :

''Gentlemen : I declare open the Fourth International Congress of Applied Chemistry. The first words which we pro-

nounce to-day in the grand amphitheater of the University of Paris, should be words of thanks addressed to the bureau of the Vienna congress. We have not forgotten the charming fashion with which we were received in the capital of the Austro-Hungarian Empire. Nor have we forgotten that the members of the last congress decided to meet here again by reason of the universal exposition which closes the 19th century. Gentlemen, you have not forgotten the date fixed. You have come in great numbers. We thank you, and we will do our best to do the honors of the city, and of that exposition which your own efforts have rendered worthy of the progress of science, and of industry. These congresses have opponents. Many see in them only occasions for excursions and banquets, more or less repeated. When I think that we have, during the exposition, 127 congresses regularly organized, in the warmest months of the year, I desire to class myself among the opponents of whom I have just spoken, but when I meet among this crowd of chemists, which fills our new Sorbonne, already too small, the smiling countenance of a friend from America, or of a delegate already known in the preceding congresses, I am happy to exchange my ideas, and class myself with those who rally to the support of the 127 congresses of our universal exposition.

"I will add that these congresse sought to have their immediate utility. Many economic questions, of which certain ones are vital for industry, can be studied by you with care and afterwards submitted to the different governments represented. The continuity of your efforts in successive congresses must lead to useful solutions. The attention with which the different governments follow your congresses is a sure guarantee to you of the interest which the public authorities bear you.

"Gentlemen, I cannot terminate these few words without addressing our best thanks to the French Government which has taken our congress under its patronage, and to the president of the republic who has honored us by being officially represented at this opening meeting. I am also to thank the ministers who, not content with sending us official delegates, have for two years done all in their power to aid our work."

M. Moissan then thanked the ministers by name, and also the learned societies, and the foreign governments, and the foreign learned societies which had sent delegates, and closed his address in the following words :

" Gentlemen, our dear president of honor, M. Marcellin Berthelot, on account of a slight indisposition from which he has suffered for several days, we have begged in your name not to expose himself to the fatigue of this first reunion, and if you will kindly permit me I will read the discourse which he has prepared."

The address of M. Berthelot, read by President Moissan, was of the greatest interest. He said in part :

" Gentlemen : I bid you welcome in the name of France and of the Republic. You have come from all parts of the world to show your works at the exposition of 1900, and to participate in that universal competition of all the industries in that pacific contest of all the people for the honor and the profit of the human race."

M. Berthelot next called attention to the fact that chemistry was the most important of the sciences which were to work for the good of the human race in the coming century ; that it did not belong to any continent, neither to Europe nor America ; nor to any country ; neither to Germany, nor to France, nor to England, but it was the common heritage of all mankind. He also developed the fact that chemistry owed little to the remote past, that it is essentially a modern science which had borrowed but little from the alchemy and necromancy of the middle ages. "Let us guard then," he said, " the belief that chemistry is the one work purely modern. In reality, it belongs to the years which have recently passed. Allow me also to retrace some of the grand historic steps of the general methods of chemistry and of their progress."

Perhaps no living chemist is better able to give in a brief review the chief characteristics of chemical science than M. Berthelot. He began his historic account by references to the chemical arts practiced in Ancient Egypt, especially in metallurgy. He called attention to the fact that the science of antiquity became also that of the modern age, transmitted in part directly by the technical traditions of the workshops and in part by the Syrians and Arabs.

It was in the central part of Europe, in the 13th and 14th centuries, that there was noticed the first assumption of the scientific spirit in its industrial initiative. It was at this time that new chemical methods made their appearance. The manufacture of metals was perfected, leading to the construction of powerful machines for war and for industry. The use of saltpeter in the manufacture of Greek fire, and of powder, created a revolution in modern warfare. The knowledge, which then became general, of fermentation and distillation led to the manufacture of alcohol on a scale sufficient to be used in the arts. Many of the essential oils of plants were also discovered about this time, and nitric, sulphuric, and hydrochloric acids became established objects of manufacture.

I could not give here even a synopsis of the rest of the address of M. Berthelot, bringing, by brief references to the principal steps of progress, the science of chemistry down to the present time. One point, especially, in speaking of the employment of fuels, is worthy of particular notice here. He said :

" It is thus seen that the employment of carbon, and of oil, the old generators of chemical energy, by reason of the heat disengaged by their union with the oxygen of the air, shows a tendency to-day to be replaced by the energy obtained by the fall of water, energy purely mechanical ; but coal and oil exist in limited quantities which are exhaustible while the falls of water are not so, because they are derived from the energy borrowed from the sun, an energy of which the human race will never see the end."

He closed his address in the following words :

" Better than mysterious magic, better than the antique faith, modern science lifts the mountains and realizes dreams and miracles. It creates without cessation riches which cannot be taken from anyone by force or by stratagem. It tends thus to the equalization of fortunes by the universal increase of capital, and the equalization of intelligence by incessant publication, liberal and disinterested, of the discoveries of learned men, and especially by the general elevation of public instruction and of workers. The hatred among men, peoples, and individuals is born of ignorance and egoism, but science exerts itself without relaxation to diminish that because it belongs neither to a private personality nor to a particular nation. It teaches us that all are citizens of the same country, that all the civilized people of the world are united. Science has no nationality. It is as well German, English, Italian, Russian, Japanese, as French. It is progressive among small nations as well as among large. Each one brings its contribution to the common work. This is the reason, I repeat, that all civilized peoples are united. Every loss suffered or inflicted upon one of them is a loss for all humanity, a loss at the same time material, on account of the destruction of existing values, and a loss moral by the weakening of the necessary bond which attaches men to one another. When these truths shall be tried by all, and shall have penetrated the minds in the most elevated social layers of the aristocracy as well as the most fundamental layers of democracy, we will have understood that the true law of human interests is not a law of conflict and of egoism, but a law of love. This is how the science which brings us together to-day in this environment proclaims as the final end of its instruction, universal solidarity and fraternity."

After the address of M. Berthelot, M. Dupont, the secretary-general, read his report as secretary of the Committee of Organization. The congress then proceeded to the formal election of officers, choosing M. Berthelot as president of honor, M. Moissan, as president, and a list of vice-presidents representing different countries having delegates in the congress. For the United States, the vice-presidents chosen were Messrs. Doremus, Rising, Chandler, Clarke, and Wiley. Among the vice-presidents of Germany were Messrs. Fischer, Maercker, and Herzfeld ; from Italy,

Cannizzaro and Piutti ; from Switzerland, Lunge ; from Russia, Mendeléef ; from Austria, Strohmer and Liebermann ; from Belgium, Sachs ; from Egypt, Ventre-Pasha ; from England, Thorpe; and from Greece, Christomanos.

At 2 o'clock in the afternoon the various sections met for organization. The organization was completed as follows :

Section 1.—Analytical Chemistry ; president : M. Muntz ; and presidents of honor : MM. Lunge and Clarke.

Section 2.—Industrial Chemistry of Inorganic Products ; president : M. Etard.

Section 3.—Metallurgy, Mines and Explosives ; president : M. Adolf Carnot.

Section 4.—Industrial Chemistry of Organic Products ; president : Lindet.

Section 6.—The Chemical Industry of Fermentations ; president : M. Durin.

Section 7.—Agricultural Chemistry ; president : M. Dehérain.

Section 8.—Hygiene and Medical Chemistry, and Chemistry of Food Adulteration ; president : M. Riche.

Section 9.—Photography ; president : M. Janssen.

Section 10.—Electrochemistry ; president : M. Moissan.

At 4.30 o'clock, M. Leygues, minister of public instruction and beaux-arts, received the members of the congress at the Sorbonne, where a lunch was prepared in their honor. M. Leygues made a happy address which was warmly applauded.

The rest of the day was devoted to a visit to the new laboratories of the Sorbonne which have lately been completely reconstructed. The laboratories especially visited were those of Troost, Haller, and Lippmann. In the laboratory of Lippmann were found many of the interesting color photographs, which he has made by means of an invention he has perfected of depositing in the original negative successive films of silver having a definite relation to the wave-length of various rays. When these negatives are viewed by reflected light, the various colors are reproduced corresponding to the wave-lengths employed in the deposition of the superimposed silver films. The method of producing these photographs has already been described in sufficient detail, but I may say here that the principle consists in placing back of the plate, which should be transparent, on which the negative is to be made, a film of mercury which, by the reflection of the transmitted rays, produces the interference necessary to secure the deposition of the superimposed silver films.

The modern appliances for increased laboratory facilities were carefully studied by the members of the congress, who were received in all parts of the building, by the professors and their assistants, the greatest courtesy and willingness to answer all inquiries being shown.

17-23

I cannot do more than mention some of the most important
papers presented to the sections on the successive days of the
meeting.

In Section 1, M. Hanriot raised the question of the assumption
as a basis for the atomic weights the value of 16 for oxygen. The
discussion of this point was engaged in by many of the members of
the section, including Professor Clarke of this country.. At the
end of the discussion, M. Hanriot proposed the following resolu-
tion : '' The congress of applied chemistry, believing that the
adoption of the atomic weight of oxygen as a basis will lead to a
greater stability, and to a simplification in a calculation of the
atomic weights, wishes to associate itself with the workers of an
international commission.'' This resolution was unanimously
adopted. Professor Clarke proposed the formation of an interna-
tional committee, having for its object to indicate to chemists the
methods which ought to be adopted, and the coefficients which
they ought to adopt in the different calculations which they make.
This proposal was also adopted unanimously.

M. Krause read a paper upon the symbols and abbreviations
usually employed in chemistry, in which he took the ground that
the symbols Am and Cy ought not to be employed to represent
the radicals ammonium and cyanogen, nor should methyl be repre-
sented by Me, ethyl by Et, nor phenyl by Ph. He also claimed
that the words ester and ether, should not be synonymously
employed. It was voted to leave that question for further study.

M. Vivier proposed the following resolution : '' There shall be
established by an international special commission a table of chem-
ical and physical constants of which the use shall be obligatory
upon all official chemists in countries represented in this congress,
and upon unofficial chemists in cases where they shall be called
as experts before any jurisdiction whatever.'' This resolution
was also adopted.

In view of the fact that at the present time a great deal of pres-
sure has been brought to bear upon our congress to establish a
bureau of standards, similar to the Reichsanstalt at Charlotten-
burg, the report presented by M. Demichel upon the graduation
of instruments of precision is of great interest.[1] This paper and
the discussion which followed, were of the usual character of
communications relating to the calibration of chemical apparatus,
and are too long for further notice.

Herr Ritter von Grueber presented to the section the work of
the commission appointed at the Third International Congress to
secure methods of uniformity, for international use, in the analysis
of fertilizers. This report was printed in English, French, and Ger-
man, and recognized, for the first time in the Congress, the progress

[1] This Bureau of Standards was established by Congress just before adjournment,
March 3, 1901.

which had been made in the United States in the analysis of agricultural products. The standard American authorities are cited in this report, in conjunction with the standard authorities in Germany and France. Since the adoption of the report pertained particularly to the section on agricultural chemistry, no formal action was taken on this resolution by Section 1. It was subsequently presented to the section on agricultural chemistry, and after an interesting debate, the proposals of the committee were unanimously adopted.

A firm basis has thus been laid for international agreement in regard to analytical methods and processes relating to the determination of the essential ingredients of fertilizer materials. This agreement is not only interesting from a scientific point of view, but also has far-reaching commercial ramifications, and will result in bringing into close touch the chemists in Europe and in the United States who have to do with imported or exported fertilizing materials.

M. Christomanos entertained the section with an account of the studies which he had made of the transformation of red phosphorus into arsenic, under the influence of ammonium nitrate. This is a theme, which has lately excited a great deal of attention. Whether or not it be true that arsenic is one of the elements which forms a compound heretofore known as phosphorus, it is too early to state. The intimate relations, however, which arsenic bears to phosphorus in all of its chemical reactions show that whether or not the two substances are forms of some original material or have entirely different natures, they surely resemble each other very much in regard to their chemical deportment.

An interesting subject to our wine-makers, was that presented by M. Chuard, of Switzerland, concerning the state of sulphurous acid in wines, and the functions which this acid performs in wine-making and ripening. It has long been known that the deportment of carbonic acid, formed by natural fermentation in the bottles, as in the making of champagne, is quite different from that of carbonic acid charged artificially into a still wine. The study of the deportment of sulphurous acid in wines may throw some light on the interesting relation which gases bear to the liquids when in solution under pressure or otherwise.

An interesting communication was made by M. Christomanos in giving the data of the analysis of a piece of iron more than 3,000 years old, which had been recovered from below the foundation of the marble column of the Acropolis at Athens. M. Christomanos also showed an interesting experiment which blackened pieces of marble without danger of fracture, by means of the flame of metallic magnesium which deoxidized a circumscribed

portion of the marble into lime and set the carbon free. He called the process " marmocautère."

Many interesting papers were also presented in Section 2.

To those interested in the analysis of food products, the paper by M. Lucian on some causes of error in the employment of the bomb calorimeter will prove valuable. If the oxygen used is obtained by electrolysis, it is apt to be contaminated with traces of hydrogen, and it is not sufficient to determine the percentage of hydrogen by combustion in a capillary tube of platinum. In the combustion of carbonaceous masses, it is not safe to assume that all the hydrogen which may be contained in the oxygen is burned. The quantity of hydrogen burned is a function of the total calories set at liberty by the combustion of the carbon and, consequently, is an unknown function. It is not possible, therefore, to calculate the error in such a case and oxygen, which is entirely free from hydrogen, should be employed.

M. Guillet read an interesting statistical paper on the inorganic chemical products of France, in which the quantities of all important chemicals manufactured in France were given.

M. Doremus, although not present himself, sent an interesting paper on fluohydric acid and the fluorides, in which he discussed the production of these important substances.

M. Perron gave an interesting paper on the sulphuric acid industry in which all the modern improvements were described. This paper was ably discussed by M. Lunge, who is recognized as the highest authority in the world on sulphuric acid production.

M. Boudouard gave an exhibition of the different pyrometric methods which are used for high temperatures. Eight different kinds were described in detail.

M. Bloche gave an historical and technical paper on the production of barium and hydrogen peroxide containing extremely useful information to those engaged in those industries or using their products. The amount of barium peroxide produced in France, is about 1000 tons annually, and the hydrogen peroxide manufactured amounts to from 2000 to 3000 tons. The chief uses of hydrogen peroxide are for antiseptic purposes and for bleaching.

In Section 3, M. Pellet gave the results of his study of the estimation of sulphur in minerals, coals, bitumens, and rubber. The principle adopted is the following : The sulphur and the organic matter are oxidized by fusion with a sufficient quantity of potassium nitrate, variable with the quality of the substance analyzed. Some pure sodium carbonate is added, in quantity usually double that of the nitrate, to moderate the action of the latter. All of the sulphur passes into the state of neutral sulphate or of soluble alkaline sulphate. The melted mass is

treated, over a flame free of sulphur, as for instance an alcohol lamp, by water, filtered, the filtered liquor acidified, some barium chloride added, heated, and again filtered. Thus, the solution of the iron, as in the case of pyrites, is avoided. The precipitation of the barium sulphate is rapid and complete. The determination can be terminated in less than an hour.

M. Le Chatelier presented an elaborate report on the state of our knowledge of the different allotropic conditions of iron and steel.

M. Barthelemy presented a résumé of legislation relating to the storing and transportation of explosives in different countries. He cited the necessity of getting a special class of explosives which are perfectly safe and which can be admitted for transport by express in cases of urgency.

M. Le Chatelier also presented a new microscope for the study of materials and for photographing the same. The description is too long for insertion here.

In Section 4, M. Thomas presented a paper on viscose, a form of cellulose, which can be used for various purposes, as, for instance, sizing paper, decorative painting, adulteration of rubber, fabrication of thin pellicles, threads, celluloid, ethers, acetates, etc.

M. Guillemare stated that all green plants digested with a weak solution of caustic soda yielded their chlorophyll in the form of sodium chlorophyllate, and for this reason he believed that chlorophyll should be known by the name of chlorophyllic acid.

M. Pierron gave an account of the catalytic heating action of platinum from the time of Humphry Davy to the present.

M. Arachequesne called attention to the fiscal regulations existing in France, and other countries, concerning the use of alcohol in the arts, and the hardships which manufacturers had to undergo, by reason of these regulations, and the requirements for denaturalization. He presented some resolutions, which were adopted, calling upon the different governments to modify their regulations in such a way as to permit the use of pure alcohol in certain cases, and where denaturalization was required to make it as inexpensive as possible.

M. Reid presented numerous specimens of a product known as velvril, intended to replace rubber and gutta percha in a certain number of their applications.

M. Ferdinand Jean presented a study of the rôle of micro-organisms in the liquors of the tannery, and in skins, and gave his experience with a number of antiseptics.

M. Kostancki gave a résumé of his work upon vegetable coloring-matters.

M. Jules Wolff gave results of the analyses of the roots of chicory. The quantity of inulin amounts to 15 per cent. in the fresh

root, but the inulin disappears almost completely during torrefaction.

In Section 5, which was the most numerously attended of any of the sections of the congress, the papers were chiefly of a technical character. Two papers were read by delegates from this country in this section, one by M. Wiley, showing the influence of temperature on the specific rotation of sugar, and the other by M. Wiechmann, taking the ground that temperature exerts no influence on specific rotation. This question of the influence of temperature on the specific rotation was also discussed before the section by M. Pellat, who gave an elaborate mathematical discussion of the data which he had obtained in his investigations.

This theme is particularly interesting to the members of the Northeastern Section, because the great influence of temperature on specific rotation was first pointed out by Andrews who, at that time, was connected with the Institute of Technology. The matter is of such importance, both scientifically and commercially, that it occupied the chief part of the time of the International Committee on Unification of Methods of Sugar Analysis. In the meeting of this committee, the data relating to the influence of temperature on polarizations were presented at length by M. Wiley of the United States, and M. Brodhun, of Germany. The only advocate of the stability of specific rotation, independent of temperature, was M. Wiechmann of the United States. The opinions of the majority were embodied in a resolution which finally passed the International Committee without a dissenting vote. This resolution was to the effect that the saccharimeter should be adjusted as nearly as possible to a temperature of $20°$, but when this is not a convenient temperature the adjustment should be made at other temperatures near that of the usual temperature of the laboratory where the polarizations are performed ; and further that all polarizations should be performed at, or as nearly as possible, the temperature at which the instrument is adjusted. The influence of temperature on specific rotation has now been so thoroughly worked out that we may say without hesitation that the points established by Andrews eleven years ago, are now fully accepted by practically all the investigators of the world.

I, perhaps, in this connection might also call attention to the fact that the two important international committees on subjects particularly associated with agriculture have made more progress in their work, and received more approval from the congress than any other committees which have been appointed. I refer to the International Committee on Methods of Fertilizer Analysis and the International Committee on Unification of Methods of Sugar Analysis. While both of these committees have been

continued for further work, the objects for which they were established have been practically attained, and the chemists of the world are now able to stand on a common foundation in two important branches of chemical analyses. This fact shows how easy it would be to unite the methods of chemists all over the world on all points connected with analytical processes.

In Section 6, there was nothing brought out in regard to fermentation as interesting as the paper read at Vienna by Buchner on fermentation without yeast.

M. Effront, the eminent Belgian authority, presented a communication on the rational use of antiseptics in the distillery, and showed that there were four factors to be considered, *viz.*: 1, the quantity of antiseptic necessary to moderate or arrest the development of ferments; 2, the quantity of antiseptic which enfeebles the yeast itself; 3, the quantity to be used without enfeebling the active substance of the malt; and 4, the influence of antiseptics upon the malts.

M. Barbet presented a communication upon the use of pure yeast in the distillery after sterilization, a subject which is now creating a great deal of interest. We are all familiar doubtless with the imitations of the flavors of wines which are produced by the fermentation of malt extracts with ferments from the wine cellar. The production of particular flavors in fermented beverages, as well as in those which are distilled, will doubtless in the near future be controlled at will by previous sterilization of the mass and the employment of especially cultivated ferments which produce distinctive flavors.

Naturally, the section in which I was most interested was Section 7 on agricultural chemistry. The subjects discussed ranged from the character of the soil to the most difficult problems of vegetable physiology.

M. Dehérain, the distinguished chemist of the agricultural station at Grignon, read a paper showing the chemical and physical effects of the cultivation of a soil in which he showed that the aeration of the soil and the destruction of weeds were not the principal points to be kept in view. The principal value of cultivation is found in the relation of cultivated soils to moisture. Soils which tend to be too wet are dried out more readily by cultivation, while those which suffer from drought have their water retained by the same means. Soils should be cultivated every year if possible. Water charged with carbonic acid dissolves chalk and causes the clay to lose its coagulability.

M. Wiley presented a paper to the section on the economic uses of corn stalks, showing the immense quantity of valuable food material for cattle, destroyed annually in the United States, by the burning of stalks of Indian corn. He showed how the cornstalk becomes one of the best absorbents for blood and

molasses, and thus would form the basis of some of the most valuable manufactured cattle foods.

M. Schneidewind laid before the section some of the results obtained at the agronomic station at Halle on denitrification and in the transformation of soluble nitrogenous compounds into insoluble.

In Section 8, interesting communications were made in regard to the falsification of wines, and it was brought out in the discussion that the *vin ordinaire* obtained at Paris was almost wholly artificial in character, about one barrel of low grade red wine serving as a basis for at least three barrels of the material placed on sale.

M. Berger gave the results of his study in the sterilization of water by peroxide of chlorine. This compound is of such great activity that a quantity less than a milligram suffices to sterilize a liter of water.

M. Ogier states that it is certain that the composition of water treated is not modified in an unfavorable sense by the peroxide of chlorine, and, in so far as mineral matters are concerned, its use does not produce an increase, except in an infinitesimal way so small as to escape detection by analysis. The water which has been sterilized is easily freed from any excess of peroxide of chlorine so that it may be regarded as an irreproachable agent from a hygienic point of view.

M. Brevans discussed the detection of saccharin in alimentary products, in which the method of Remsen was given the preference. As is well-known, the use of saccharin is prohibited in most European countries. Its use in this country by diabetic patients has grown to large proportions. It is extremely doubtful if it serves any useful purpose, while it is quite certain that it hinders digestion. Its general use should be regulated by law, and physicians should be admonished not to prescribe it promiscuously to their patients and never to any particular one for any length of time.

M. Halphen gave a report on the adulteration of oils, and the methods of detecting them.

MM. Abelous and Gerard presented a paper in which they described a soluble ferment found in animal tissues producing nitrates. It exists in the greater number of organs although the proportion is unequal. It not only produces nitrates, but decolorizes the blue of methylene. The ferment has its maximum activity at between 40° and 50°, and is destroyed at about 71°.

M. Molière pointed out the conditions in which it is necessary to work to obtain a regular determination of glycogen in normal and pathological tissues and pointed out the steps necessary to extract the glycogen from the tissues and precipitate the nitro-

genous matters and finally to separate the crude glycogen. The real quantity of glycogen is determined according to the weight of suboxide of copper given by the crude product hydrolyzed by sulphuric acid of 2.5 per cent. strength, and the heated product permitted to act upon Fehling's solution.

The whole subject of the determination of glycogen has lately been studied in the Department of Agriculture, by MM. Bigelow, and Haywood, with the result of showing that the method which is described above and which has been practiced for many years is not reliable. The results of these investigations will soon be published for the information of chemists interested in the determination of glycogen.

I have in the above brief résumé only touched upon some of the papers which to me were of superior interest. Another reviewer would doubtless have selected quite a different series of papers for mention. At any rate, the above will show the general character of the papers which were read, numbered as they were by the hundreds, and of the character of the discussions in regard to them. Of course it is not possible for anyone to be present at all the sections, and it is quite likely that many of the most interesting papers escaped my attention entirely.

I have already called attention to the remark made by M. Moissan in his opening address, to the effect that one of the most valuable points connected with an international congress is the opportunity which it affords of making the personal acquaintance of our professional brethren whom we have long known from their works. And so it seems to me that the most delightful as well as the most useful part of the congress was the meeting of old friends and the making of new ones, especially those whom we had known before by correspondence or otherwise.

In the absence of M. Berthelot, unhappily detained by a slight indisposition from attending the meetings of the congress, by far the most interesting figure to my mind was that of Mendeléef, of St. Petersburg. His white flowing hair and attractive countenance marked him everywhere as a man of distinction. He takes the greatest interest in the work of the chemists of this country, and spoke particularly of many of the contributions which our chemists have made to science. While we may not regard Mendeléef as the first originator of the theory of the periodic law, that being reserved to the honor of Newlands, he must be accorded the credit of having developed it in a thoroughly philosophical and practical way. Among foreign chemists, Mendeléef's work in explosives has been of the highest character and many of the smokeless powders made to-day are composed directly according to his formula or with very little variation therefrom. In fact, Mendeléef has covered almost the whole field of chemical research and, among the older men, shares with Berthelot and Crookes,

the honor of being probably the most eminent chemist now living.

Among the representatives from Germany, perhaps the most distinguished and certainly the most striking in form and figure was Otto Witt, our friend of the Chicago exposition, not less ponderous of figure, not less genial of disposition than at that time. Dr. Witt occupied a high position in the German commissions standing, I believe, next to the director-general and his assistant and was, by all odds, with the French, the most popular German representative. His well-known ability, and his suavity and tact pointed him out as the proper person to be named as president of the Committee of Organization of the next congress, which is to be held in Berlin in 1902.

From our country we had the distinguished president of the Society of Chemical Industry, Professor C. F. Chandler, of New York, who represented, with dignity and success, the advance guard of American applied chemistry.

The chemists of England were conspicuous by their absence. In this congress, as in all the others, scarcely an Englishman was to be found.

Switzerland sent M. Lunge, whose name is known wherever applied chemistry is practiced as being at the head of his profession.

From Italy, we had as a delegate M. Cannizzaro who not only is distinguished in the field of chemistry, but is vice-president of the Italian Senate. In fact the scientific men of Europe do not think it is beneath their notice to take an interest in public affairs and many of them, as in the cases of Berthelot and Cannizzaro, occupy the highest public positions.

From Austro-Hungary the principal representative was the genial Frederich Strohmer, the secretary-general of the Vienna Congress, who did so much at that time to make the sojourn of the foreign delegates in the capital of Austria, pleasant and profitable.

From Greece, M. Christomanos headed the list of delegates.

The distinguished men from France, of course, were numbered by the dozens. In addition to those who have already been named, it was especially pleasant to meet Dehérain, Lindet, Troost, Haller, Lippmann, and others equally as famous.

The Committee on Organization of the Congress showed a great improvement over those of former congresses in the care taken to have inscribed and identified the delegates from foreign countries. Not only was a list of all these delegates published in the daily program, but, what had never been done before in these congresses, the Paris address of each one was affixed, thus rendering it possible to communicate with these delegates in case they could not be met at the sectional meetings which, on account of the widely separated localities in which these sections met, was always a difficult matter.

Highly contributory to the good fellowship and intimate acquaintance were the luncheons, breakfasts, excursions, and banquets offered by the members of the congress to the delegates of foreign governments and learned societies.

At midday of the first day of the meeting, the congressists separated into groups of friends, and took breakfast at the different restaurants in the Latin quarter, in the neighborhood of the Sorbonne. The restaurant of La Société Savante served a special breakfast for members of the congress.

The reception given at 4.30 o'clock the same day by M. Leygues, minister of public instruction, has already been noticed.

On the second day of the meeting a breakfast was given at the Restaurant Lyonnaise of the exposition, Champs de Mars, under the presidency of M. Henry Boucher, member of the Chamber of Deputies and former minister of commerce. At the dessert M. Moissan proposed the health of the science of chemistry in a happy address in which he said:

"There was in antiquity a god who was called Janus. He had two faces, one sad, the other gay, so placed that one might choose that which was adapted the best to his impressions. Chemistry is somewhat like Janus. She has two faces. There is a good chemistry and a bad. The Phoenicians with great difficulty obtained a mineral from the Cassiterite Islands from which they obtained tin which they afterwards adulterated with lead. Chemistry has discovered mineral colors in order to add as much as possible to them of barium sulphate. Chemistry has given us the aniline colors which tint our silk in such pleasant variations and, at the same time, she has taught certain adulterators to add to the silk, 90 per cent. of foreign matter. Chemistry has taught us to obtain as much sugar as possible from the cane and the beet, but she has also invented saccharin which is used for fraudulent purposes. As to wines, I may permit myself to say that certain ones have been adulterated, but we have not noticed that to-day for we have not drunk chemical wines. Yes! by the side of every new preparation is found its falsification. Alas! this is the eternal history of life, the bad is mixed with the good and the fable of Æsop is always true. Chemistry might then be compared to the sabre of M. Prud'homme which might serve to defend our institutions, and, in case of need, to fight them; but she has an advantage over that historic sabre and that is, it is she who aids us in pursuing the adulterators. It is by her trials, by her methods, by her analyses, often very delicate, that we are able to detect the fraud. Chemistry thus heals her own wounds. In the last place, we are able to stop with this consoling thought that if in chemistry virtue is not always rewarded, at least vice is often punished. Gentlemen, I drink to the good chemistry."

The closing banquet of the congress was held at the Hotel

Continental, on the evening of July 28th, when about 300 members
sat down to a dinner.

The banquet was presided over by M. Leygues, the minister of
public instruction, having on his right M. Moissan, and on his
left M. Cannizzaro.   It is needless to add that the cuisine was of
the most exquisite kind, the wines of the best vintages and served
at the proper temperatures, and the good fellowship of the com-
pany was equal to the elegant repast which was served.

M. Moissan at the close of the dinner proposed the health of
the president of the republic, and of the minister of public instruc-
tion and to this toast the minister of public instruction, in the
name of the president, and in his own person made a most happy
reply.

By arrangement of the delegates of foreign countries M. Lunge
spoke for them in an eloquent discourse praising the hospitality
of the French and expressing his great satisfaction in having
been present at the inauguration of the statue of Lavoisier.   He
expressed great satisfaction in knowing that the United States
and Europe are united, if not in the domain of politics, at least
in the domain of science.   He drank to the solidarity of the
nations united by science, and to the success of the International
Congresses of Applied Chemistry, and to the health of M. Moissan
to whom he wished a long and successful career.

Numerous personally conducted tours through the most inter-
esting parts of the exposition were enjoyed under the guidance of
experts thoroughly acquainted with the character and extent of
the exhibits.   By this means the congressists were able to see, at
small expense of time, the most interesting of the chemical
exhibits.   While, of course, in magnitude the French exhibits of
chemical products were more extensive than those of any other
country, it must be conceded that the German exhibit was supe-
rior in arrangement, beauty of design, and completeness of detail.
Our own chemical exhibit was of a very modest nature and while
it was excellent, in so far as it went, it did not in any way illus-
trate the great strides which our country has made in the last few
decades in manufacturing chemistry.   Our people are doubtless
so busy in the conduct of their great manufacturing problems that
they do not think it worth while to give their time and money to
securing adequate representation in foreign expositions.   In this,
however, I think they make a great mistake, and let us hope that
when another World's Exposition takes place in a European cap-
ital, American chemical products will be represented on a scale
commensurate with their commercial magnitude.

The visit to the Pasteur Institute was full of interest, espe-
cially to those congressists who had not had a previous opportunity
of seeing this monument to the greatest of modern savants.   Pas-
teur was peculiarly and practically a chemist, and the whole suc-

cess of his career must be attributed to his early training in our science and to his constant practice of it. His late researches in the study of toxines produced in diseases and the best methods of preventing them, were largely of a biochemic nature, and his efforts were made possible by his previous training. He, indeed, would be incapable of higher feeling who could look upon the crypt which contains the mortal remains of this great man without a feeling of gratitude as well as of awe: awe in the presence of the mortal remains of so great a life, and gratitude that that life still persists in the benefits which science, under its skilful hand, confers upon .suffering humanity. The scientific establishment of the principle of vaccination as applied to other diseases due to toxines was made possible by the works of Pasteur, and these works offer for the future the expectation that in the progress which will certainly be made along these lines many of the plagues which have in the past decimated nations may be wholly eradicated, or at least brought under control.

Through the munificence of the city of Paris, and of Baroness Hirsch, a magnificent addition to the Pasteur Institute is now in construction, across the street from the old building, which will be devoted exclusively to physiological and pathological studies, especially physiological chemistry.

Joined to these laboratories is a hospital built upon the most approved modern plans. The Pasteur Institute is to-day one of the greatest scientific establishments in the world, and of all the schools of biology and physiological chemistry, it is the one where the experimental method is the most fully developed. Thanks to the increase of its buildings, it will be able to receive a greater number of pupils than ever before, and thus to satisfy the immense demand which has been made upon it up to the present time.

Thus the labors of this great man will continue through the twentieth century, and no one can estimate the blessings which they will secure in immunity from disease, in longer life, and in sustained powers of labor, and enjoyment for the whole race.

All the members of the congress are under lasting obligations to M. Duclaux, the director, and to M. Roux, the assistant director, who so amiably performed the honors of this great establishment.

Returning from the visit to the institute, the congressists were received by the préfect of police, and the préfect of the Seine, at the Hotel de Ville. There the congress was addressed by the president of the municipal council who, in a happy speech, welcomed the members of the congress to the city hall, and in a few well-turned phrases jocosely alluded to the differences which exist between the municipal government and the Elysée Palace. Our own people will understand better the strain which exists

there when they know that the municipal government of Paris is in the control of a political party which is violently opposed to the present republican form of government and these relations are so drawn that the president of the municipal council no longer attends the functions of the president of the republic.

The most charming of the excursions made by the congress was a visit to Chantilly. The chateau and estates of Chantilly were formerly the property of the famous Condé, the great constable of France, and in a direct line of descent were inherited by the junior branch of the Bourbons of which the late Duc D'Aumale was the last representative. Dying in 1898 without heirs the Duc, by a will dated October 25, 1886, left this vast estate,—the chateau and its grounds, its fountains, its buildings and forests, its books, pictures, and objects of art, to the French Institute to hold in trust forever for the benefit of the French people and the people of the whole world. This patriotic man, although of royal descent, was one of the few princes of the blood who gave a genuine adhesion to the republican form of government, and he attested his devotion to his country, even as a republic, by leaving to it this magnificent estate with all its priceless objects of art and of history.

All too short were the few hours which we were able to spend in that magnificent palace, filled with treasures the equal of which can no where else be seen, when judged from the point of view of history. Although the day was extremely hot, no one suffered from fatigue with such a prospect as was presented. The chateau, the museums, the lakes, the fish ponds, the race course, the meadows, and the magnificent stables, which are the admiration of the world, all helped to make the afternoon delightful.

One of the most pleasant features in connection with the congress was the unveiling of the statue of Lavoisier in the Place de la Madeleine, under the auspices of the French Academy of Sciences. A beautiful canopy had been erected for the foreign delegates and invited guests, and, although the day was exceptionally hot, there was no lack of interest in the exercises. Nearly all the members of the congress were present to render honor to the great founder of their science, and it was in the midst of an audience composed of those learned men, of the Academy of Sciences, of the representatives of the other branches of the institute, and of numerous learned societies of France, and foreign countries, that the statue of the founder of the science of chemistry, of immortal memory, as Wurtz has said, was unveiled. This beautiful piece of sculpture represents Lavoisier with uplifted right hand in the attitude of delivering a lecture to his students. The left elbow is supported upon a lot of apparatus representing the original forms used by Lavoisier in his immortal discoveries. The piece of statuary bears the simple inscription

"Lavoisier, 1743–1794." This piece of sculpture is the work of one of the greatest of contemporaneous artists, Barrias. It can be said without exaggeration that it adds greatly to his glory. Barrias has shown us the master in all the majesty of his genius and, at the same time, in the garb of the philosopher and incomparable experimenter.

Orations were pronounced by Berthelot, in his absence read by M. Moissan, and by Leygues, the minister of public instruction. The discourse of M. Leygues was especially eloquent. He closed his address with the following words :

" There is an invincible force in things which always triumphs in the end. The scientific institutions which seemed to have disappeared forever with Lavoisier soon sprung up again vivified and rejuvenated by the powerful breath of the revolution, and remain reflected in our glorious institute of France. Among us the rights of free thought are imprescriptible. Nothing can prevail against them. Lavoisier was brave in the face of death. 'I have obtained,' he wrote to Augez de Villers, ' a career tolerably long and above all very happy, and I believe that my memory will be accompanied with some regrets, possibly even with some glory. What could I desire more? The events in which I find myself enveloped are probably going to save me the inconveniences of old age. I shall die perfectly whole. That is an advantage which I ought to count among the number of those with which I console myself.' A single remark is to be made in answer to these last words. Men like Lavoisier never wholly die, and the scaffold only serves to build a pedestal upon which grateful generations will sometime erect their images.''

To my mind there could be no happier way of stating the present attitude of the French people toward those great men whom the fury of the terror conducted to the scaffold a little over a hundred years ago. To me, there are no more interesting works of art in the great city of Paris, the mother of modern art, than the two statues of two men beheaded during the revolution, Danton, representing the spirit of pure democracy, and Lavoisier representing the spirit of pure science. His judges would not listen to his plea for a few days more of life to finish some scientific work upon which he was engaged. They hurried him with all haste to the scaffold, and now the whole scientific world unites to honor his undying memory which an ignominious death has only helped to make more precious.

H. W. WILEY.

NOTES.

Power Laboratory Ore Grinder.—In such a laboratory, as that of the Edgar Thomsen Steel Works, where many ore and slag analyses are made daily, and rapid work is essential, the question of obtaining comparatively large amounts of the samples in a fine powder is an important one. It is a general rule, in ore and slag work, that the finer the sample is ground, the more rapidly and satisfactorily can the analysis be made.

In recognition of these facts, we some time ago installed in our laboratory, a small ore grinder operated by an electric motor, which, as it does the work much more satisfactorily than was possible by hand grinding, we think worthy of description for the benefit of other chemists.

The accompanying cut shows fairly well the general appearance of the grinder. It stands 18 inces high and occupies about 1 square foot of floor space. Preferably it is made of bronze and steel, heavily nickel-plated to resist the laboratory fumes. The motion is communicated to the grinder by a ¼ inch round belt running in a grooved pulley about 4 inches in diameter. Inside the hollow mandrel thus moved, is a sliding steel rod, with a groove cut lengthwise, in which a hard-ened steel pin, fastened to the hollow mandrel, slides.

The agate pestle is fastened to this sliding rod about 1 inch from the center and at such an angle, that in revolving, it follows closely the level of the bowl of the mortar.

The pressure is regulated by a spring pressing on the top of the sliding rod. The motion of the pestle is produced by a ball and socket joint, giving a combined rocking, rolling, and scraping motion, similar to that used in hand grinding, but on account of the rapid motion and uniform pressure, is much more efficient. In order to bring all the ore, in turn, under the

pestle, the mortar is given a slow revolving motion, while a scraper, pressing against the bowl, brings all the ore under the pestle. The mortar is held in place by four thumbscrews in four posts suitably placed to hold the sides of the mortar. One of these posts can be dropped down when the set screw is loosened, which allows the mortar to be taken out, the pestle being previously pushed up about 1½ inches. This is all done in a few minutes, it not even being necessary to stop the revolution of the pestle. The power required to operate this grinder is small and could probably be obtained from a small water motor, if electricity is not available. We have four of these grinders in daily use. Leather belts can be used for connections, but after trying several kinds we find the steel spring belt is best.

<div style="text-align:right">C. B. MURRAY.</div>

EDGAR THOMSEN STEEL WORKS.

Loss of Sulphur in Preparing Ash of Plants.—It is generally known that the sulphur contained in an ash does not necessarily represent the sulphur content of the plant. Berthelot[1] states that the determination of phosphorus and sulphur when the plant is burned to an ash is often incorrect, and discusses the conditions theoretically necessary that no loss take place.[2] S. Bogdonow[3] states that the estimation of the sulphur content of a plant by determining the sulphur in the ash, is incorrect. He determines the sulphur in the plant preferably by the method of fusing it with caustic potash and potassium nitrate. Comparing his analyses of cereals made by this method with Wolf's tables of ash analyses, he concludes : (1) That the sulphur in the ash does not give even an approximate idea as to the sulphur in the plant; (2) that plants contain considerably more sulphur than has been supposed; (3) the sulphuric acid of the soil is of practical importance. It may be added that he found fertilization with sulphates advantageous to certain Russian soils.

The following experiments were made to test whether sulphur was lost on incineration of vegetable substances. No case was

[1] Compt. rend., 128, 17.
[2] Wiley ("Principles and Practice of Agricultural Analysis," Vol. III, p. 37) states, that unless special precautions are taken, a portion of the organic sulphur and phosphorus may escape during the combustion. The method of determining sulphur in protein is described : Same volume. p. 446.
[3] J. russ. phys. chem. Ges., 31, 471.

found in which all the sulphur of the plant was contained in the ash.

The determination of the sulphur was made by two methods : *a*. 10 grams were burned to an ash at the lowest possible temperature, and the sulphur determined in it ; *b*. 10 grams substance were burned with the addition of 20 cc. of a solution of calcium acetate containing 29.2 grams per liter, as recommended by Dr. A. E. Shuttleworth.

SULPHUR FOUND IN PLANTS.

	b. Burned with calcium acetate. Per cent.	*a*. Alone. Per cent.	Loss. Per cent.
Oat straw	0.158	0.151	4
Crimson clover hay	0.173	0.137	28
Green rape..............	0.503	0.471	6
Wheat bran	0.055	0.000	100
Corn silage.............	0.098	0.082	16
Timothy hay	0.085	0.076	11
Cottonseed meal........	0.222	0.071	68
Soy beans...............	0.161	0.091	58
Linseed meal...........	0.091	0.038	58

The sulphur obtained when the ash was burned by itself is from 4 to 100 per cent. less than when burned with calcium acetate. Whether the calcium acetate retains all the sulphur or not, is a point which requires further study.

The differences in the above table may in some cases seem insignificant, but owing to the quantity of material employed, it requires 0.0007 gram barium sulphate to produce a difference of 0.001 per cent.

It is plain that the determination of sulphur in an ash prepared in the usual way, far from giving any idea as to the sulphur in the plant, may prove very misleading. Any conclusions drawn from such analyses are liable to prove erroneous.

This work was performed in the laboratory of the North Carolina Experiment Station, with the permission of Professor W. A. Withers, chemist.

G. S. FRAPS.

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A Simple Test to Distinguish Oleomargarine from Butter.—In the March (1900) number of this Journal, Hess and Doolittle refer

to the well-known spoon test for oleomargarine and in the October number Dr. C. A. Crampton mentions the fact that this test is preferred to the polarizing microscope by many revenue examiners.

Another simple test was called to my attention by Mr. C. H. Waterhouse, Dairy Instructor at the New Hampshire College, a short time before his death, this last summer, and was originated by him. Previous to his sickness he had asked me to try it on various kinds of fats, but until recently I had been unable to do so. From the results now obtained and the simplicity of the test, I am convinced that it may find application preliminary to chemical analysis.

The details are as follows: Half fill a 100 cc. beaker with sweet milk, heat nearly to boiling and add from 5 to 10 grams of butter or oleomargarine. Stir with a small rod, which is preferably of wood and about the size of a match, until the fat is melted. The beaker is then placed in cold water and the milk stirred until the temperature falls sufficiently for the fat to congeal. At this point the fat if oleomargarine can easily be collected together into one lump by means of the rod, while if butter it will granulate and cannot be so collected. The distinction is very marked. The stirring is not, of necessity, continuous during the cooling, but it should be stirred as the fat is solidifying and for a short time before. The milk should be well mixed before being turned into the beaker as otherwise cream may be turned from the top and contain so much butter-fat that the test is vitiated for oleomargarine. I have tried this test many times on twenty-one different samples of oleomargarine and on several samples of butter and have found it to work in every case. Many of these samples were also given by me to my assistant for trial and he never failed to immediately distinguish between oleomargarine and butter. I have also made mixtures and have found that one containing about 25 per cent. or less of butter would be always classed as an oleo. Lard and cottolene act the same as oleomargarine.

While the small number of samples of oleo to which the test has been applied will not allow of a positive statement of its universal application, I am convinced from my own experience that

it will prove of value, especially in the hands of revenue agents and others employed in detecting illegal sales of oleomargarine, as it may materially lessen the number of samples to be sent forward for the final proof of chemical analysis.

If this test is found to be of use it should be known as the " Waterhouse Test."   CHARLES LATHROP PARSONS.

BOOKS RECEIVED.

A Contribution to the Pharmacognosy of Official Strophanthus Seed. By Pierre Élie Félix Perrédès, B.Sc.   The Wellcome Chemical Research Laboratories, 6 King Street, Snow Hill, London, E.C.   36 pp.

Lehrbuch der anorganischen Chemie.   von Prof. Dr. H. Erdmann. Zweite Auflage. Mit 287 Abbildungen, einer rechen Tafel und sechs farbigen Tafeln.   Braunschweig : F. Vieweg & Sohn.   8vo.   xxvi + 758 pp.   Price, 16 M.

Report of the Committee on the Protection of North American Birds for the year 1900.   Extracted from the *Auk*, January, 1901.   37 pp.

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THE MEASUREMENT OF GOLD AND SILVER BUTTONS IN QUANTITATIVE BLOWPIPE ASSAYS.

BY JOSEPH W. RICHARDS.
Received February 2, 1901.

WHEN Harkort, a Freiberg student, invented the quantitative blowpipe assay for gold and silver, in 1824, he was at once confronted with the impossibility of weighing the very small buttons obtained. He surmounted the difficulty by assaying a silver ore repeatedly in the muffle, until he knew with exactness its contents. Then he assayed a standard weight of it by the blowpipe and obtained a button of a certain size whose weight was known from the amount of ore taken. Taking half and a third and a quarter of the weight of ore he obtained smaller buttons of known weight. With these he constructed a scale. He drew two fine slightly diverging lines on white cardboard, placed the buttons between the lines at the points where they fitted, and marked opposite those points the corresponding weights, or, rather, the corresponding silver contents of the ore, assuming a standard weight taken for assay.

Harkort brought the method to the attention of Plattner, the professor of metallurgy at Freiberg, and published his results at his own expense in a small book entitled "Silverprobe vor dem Löthrohr," Freiberg, 1827.

Plattner took up this method in his regular course of instruction, and improved and extended it. One of his principal improvements was the construction of the button scale ruled on ivory, made by the mechanic, August Lingke, at Freiberg. To fix accurately the dimensions of this scale, Plattner assayed a very rich silver ore repeatedly in the muffle until it was known with certainty to contain exactly 3.48 per cent. of silver. He then made repeated blowpipe assays of this ore, obtaining buttons very close together in size and weight. The two lines were then drawn on ivory so that they diverged approximately the diameter of these buttons in 150 millimeters. The buttons were then fitted exactly between the lines, and the point marked 50, the

distance from here to the meeting point of the lines being divided into fifty equal divisions. The exact dimensions of the scale as thus made were 156 mm. from 0 to 50, and the lines 0.9 mm. apart at 50. The weights corresponding to the various numbers were calculated from the number 50 representing 3.48 milligrams of silver (when 100 mg. were taken for analysis), using the assumption that as the buttons were nearly spheres, or, at least, were homologous in shape, their weights would vary as the cubes of their respective horizontal diameters. The weight of the silver button corresponding to any number from 1 to 50 would be therefore $3.48 \times \left(\dfrac{n}{50}\right)^3$, and thus these weights were all calculated and engraved on the scale opposite the numbers. A similar set of weights was obtained in an exactly similar manner for gold buttons. Thus the Plattner ivory scale was devised and is still used more extensively than any other method of measuring these small buttons.

The defects of the Plattner scale may be enumerated under the heads of :

1. Errors in construction.
2. Errors in using.

The errors in constructing the scale may be as follows:

a. The lines are sometimes not mathematically straight.

b. The lines may be rough or ragged.

c. The lines may not meet exactly at the point marked zero.

d. The lines may not be exactly the right distance apart (0.9 mm.) at the point marked 50.

It is seldom that the best scales made in Freiberg are free from one or more of these defects ; I do not believe that more than one out of five is perfect.

The errors in using the scale consist of:

a. Placing the button too high or too low through optical illusion. The button should be tangent to the inside of the lines, and in a strong light the white metallic surface of the button is difficult to see on its outer edge. One investigator has even proposed putting the silver buttons a short time into ammonium sulphide, so as to blacken them and thus facilitate their measurement.

b. Placing the button too high by virtue of parallax, which projects the middle diameter of the button against the scale on which it rests, and makes the button seem to fit higher up than its real diameter. The remedy for this is to sight first down one side of the button, then down the other, each time looking perpendicularly to the scale. This operation is tedious, and takes considerable experience.

c. The button being nearly round, it takes considerable time, patience, and experience to get it to a certain spot on a flat surface. This is not an error of the scale, but an unavoidable inconvenience, which becomes accentuated if the ivory warps, so that the scale does not lie level. A beginner will frequently make a greater mistake in measuring a button than in getting it.

Goldschmidt's Method.—Dr. V. Goldschmidt, of Heidelberg, proposed two improvements :

1. To Remelt the Cupelled Buttons on Charcoal.—This gives to them a more nearly spherical and more uniform shape than is obtained on the cupel. The button is to be removed from the cupel, hammered flat between paper, to clean it, and then touched with the reducing flame, on charcoal, just long enough for it to melt and take the spherical form. Buttons thus remelted will be heavier than cupelled buttons of the same horizontal diameter, and, therefore, heavier than the given weights on the Plattner scale.

2. Measuring the Horizontal Diameter of Such Remelted Buttons Under the Microscope.—For this purpose, a divided scale is put into the focus of the eyepiece of a compound microscope magnifying 50 to 100 diameters. A scale of 40 divisions is very suitable, the tenths of each division being estimated when measuring. The buttons are placed on a glass plate, a piece of blue glass gives a nice background, and since they come to rest only on their bases, the horizontal diameter is always in position to be measured. The diameter being known in whole divisions and tenths, reference to a previously constructed table gives the volume and weight of the button, when of gold or silver.

To construct this table, the following ingeniously devised plan was worked out by Goldschmidt : A number of bits of pure gold are melted on charcoal. The buttons obtained are each measured separately, in divisions on the scale. All the buttons are then weighed together, as accurately as possible. The total weight, divided by the specific gravity of gold, gives the sum of the volumes of the buttons. This latter, divided by the sum of the cubes of the separate diameters (expressed in divisions on the scale), gives a function μ. This function is the factor by which to multiply the cube of the diameter of any button to get its individual volume. Expressed algebraically, the above operations are:

$$\frac{\Sigma \text{ weight}}{\text{Sp. gr. gold}} = \Sigma \text{ volumes.}$$

$$\frac{\Sigma \text{ volumes}}{\Sigma \text{ (diam.)}^3} = \text{a function} = \mu.$$

Volume of any button $= \mu \times (\text{diam.})^3$
Weight of a gold button $= \mu \times$ sp. gr. gold $\times (\text{diam.})^3$
Weight of a silver button $= \mu \times$ sp. gr. silver $\times (\text{diam.})^3$

From the above data, a table can be constructed showing the weights of gold or silver buttons for every division of the scale up to its full range.

It should be remembered that measurement under the microscope is a very satisfactory laboratory method, but as it requires a compound microscope, it is not suitable for field use or prospector's outfits.

Richards' Scale.—The writer adopts Goldschmidt's idea of remelting the button on charcoal, wherever practicable, but has

devised a modification of Harkort's method for measuring the buttons.

The idea is to make two metallic edges perfectly straight, lying on a flat surface, touching each other at one point and held apart at the other extremity by a set-screw, so that the point 100 may indicate a fixed width or separation of almost exactly one millimeter. In reality, the button whose horizontal diameter fits at 100 has a diameter of 1.02 millimeters, but this distance has been so chosen that the volume and consequently the weight of said button are exactly that of a perfect sphere whose diameter is one millimeter. The other numbers on the scale have the same significance; for example, the button whose horizontal diameter fits at 43.5 has the volume and weight of a sphere whose diameter is 43.5 hundredths of a millimeter, and such is the basis on which the table is calculated.

In using the scale, the button is put into the groove, the scale inclined slightly and tapped until the button wedges itself. The tenths of a division are estimated, taking the points where the sides of the button touch the scale as the reading. As the button may sometimes roll with its shorter vertical diameter across the scale, several readings are taken and the highest reading occurring with regularity is the true horizontal diameter. For instance, among 43.4, 43.4, 41.6, 43.5, 41.8, 43.5, it is evident that 43.5 is the horizontal diameter and 41.6 or 41.8 the vertical. The button can also be observed under the lens, to see how it is lying, at any given reading.

A gentle spring keeps the right-hand strip against the set screw, thus allowing it to be pressed back for cleaning out the slot with a brush or removing a button. The scale is made of hardened aluminum, for lightness, and is set in a velvet-lined leather case. It is made by Williams, Brown, and Earle, of Philadelphia, and sold at the same price as the imported ivory Plattner scales. P. Stoë, of Heidelberg, makes and sells the scales in Germany.

The advantages of this method of construction over the engraved ivory scale are:

1. The edges are perfectly straight, from the method of construction.

2. They meet exactly at the zero point and can be adjusted to the exact distance at 100.

3. The reading is more or less automatic, the errors of placing, parallax, and personal equation being almost entirely eliminated.

The scales are adjusted by the makers, but, if by accident they get out of adjustment, a small rod of wire furnished with each instrument, whose lower end marks a given reading on a correct instrument, provides the means of quick readjustment.

Measuring Gold-Silver Alloy Buttons.—When the button obtained is pure gold or pure silver, any of the above methods give its weight directly. If, however, it is an alloy of the two, and is too small to weigh satisfactorily, but must be measured, the question of determining the silver present as well as the gold is a difficult one. The determination is very much facilitated by using the small case of standard alloys designed by Dr. Goldschmidt, of Heidelberg (made by P. Stoë, Heidelberg, imported by Williams, Brown, and Earle, Philadelphia). This is a small tablet in a brass case, containing small flattened buttons of gold-silver alloys, every 1 per cent. of silver to 20, then every 2 per cent. to 40, and every 4 per cent. to 56, where the alloy becomes silver-white. In using, the alloy button to be tested is hammered flat between paper, put on the plate and examined under the lens by diffused daylight. With a little experience, the button can be placed to one alloy. The observation gives the per cent. of silver in the button. Assayers working by the muffle will also find this a very convenient instrument to save parting where a quick, approximate determination is wanted, or to determine how much silver to add to an alloy to get the right proportions for nitric acid parting.

I have classified the different methods available to the blow-pipe assayer as follows :

I. If the button is over 50 per cent. of gold, and therefore colored, melt on charcoal, measure, and note its *volume*. Then proceed by either of the following methods :

(*a*) Flatten out, compare with the standard alloys, and get the per cent. of silver in it. From the table of specific gravities of gold-silver alloys take the specific gravity. Multiply the *volume* of the alloy by its specific gravity ; the product is its weight. From the known percentage of silver and gold in it, calculate their respective weights.

(*b*) Melt the button with a button of pure silver having an equal diameter, if the color of the alloy is pale ; or of 25 per

cent. greater diameter, if the color is brass-yellow ; or of 50 per cent. greater diameter, if of nearly pure gold color.   Hammer out flat, and part with nitric acid in the usual way.   Wrap the gold in a small piece of pure lead foil, cupel, remelt, measure, and thus get its weight and note its volume.   Subtract the volume of the gold from the volume of the alloy, and the differ-ence is the volume of the silver.   The weight of silver corre-sponding to this volume is obtained directly from the table.

The writer has verified these two methods of procedure, and found them both reliable.   The principle of method (*a*) is due to V. Goldschmidt, but not exactly in the simple form given above.   The principle of method (*b*) is based on the fact that gold and silver neither contract nor expand in alloying, which fact the writer has verified by experiment and calculation.

II. If the button is less than 50 per cent. gold, and, therefore, silver colored.   Melt on charcoal and note its *volume*.   Then proceed by either :

(*a*). Part with nitric acid (remelting with more silver if not attacked).   Wrap the gold in lead foil, cupel, remelt, measure, note its weight and volume.   Subtract its volume from that of the alloy, getting the volume of the silver, and thence its weight.

(*b*) Measure accurately a pure gold button of approximately the same diameter as the alloy button.   Melt together on char-coal, and measure carefully, noting the *volume*.   Flatten out the color will be yellow), compare with the standard alloys, and, knowing the volume, compute the weight of gold and silver present.   The weight of gold found less the weight of the gold button added, gives the weight of gold in the original assay button.   The weight of silver may be obtained by calculation from either the original alloy button or the yellow one after gold had been added.

This method of procedure was suggested by Professor B. W. Frazier, of Lehigh University.

(*c*) Replace on charcoal, and heat intensely in the point of the oxidizing flame.   The silver slowly volatilizes, and in one to five minutes the alloy becomes yellowish.   It is difficult to drive all the silver off, as the last five or ten per cent. volatilize slowly and probably also take a little gold with them.   It is best to stop when the alloy has a pronounced yellow color, measure, note the volume, flatten out, compare with standard alloys, and calculate

the weight of gold present. Take the volume of that weight of gold from the table, subtract from the volume of original alloy button, and thus obtain the volume and thence the weight of the silver.

The fact that silver can be volatilized from gold in this way, on charcoal, was described by the writer in the *Journal of the Franklin Institute*, June, 1896.

The writer finds methods I (*a*) and II (*c*) the most suitable for field work; the parting with nitric acid is preferably a laboratory method, and is the most accurate.

Note on the Quantitative Gold or Silver Assay.—The writer makes the fusion on charcoal in preference to a Freiberg carbon crucible, which is often unobtainable. When finished, it is always possible to make the slag quite liquid and then to pour out the lead *in toto*, leaving only clean slag on the charcoal. At first, it will be best to pour out on a cold steel anvil or plate, whence the lead may be picked up and placed at once on the cupel for scorifying. The writer has frequently poured the lead directly from the charcoal on the previously heated cupel, and then commenced immediately to scorify, sometimes without even allowing the lead to set. This will usually succeed for one with a steady hand, and several minutes can thus be saved.

In scorifying, if the blowpipe-tip is advanced almost to the nearer edge of the flame, an oxidizing flame of great power without a well-defined point is obtained, before which the lead oxidizes with great rapidity. 1800 mg. of lead were thus scorified to 300 mg. in two minutes; and, in general, one-half to two-thirds of the time usually consumed in scorification can be saved.

For fine cupellation, it is not absolutely necessary to pre-heat the cupel. The button is placed on the freshly struck cupel, a spot under the button strongly heated, on which the button drops as its melts. Then the cupel is turned slowly, keeping the button half-way up the far side, and the flame always heating the cupel just under it, which is thus dried before the button comes onto it.

By using such devices as the above to save time, the gold or silver assay may often be run through in from ten to fifteen minutes, with an extra five minutes for separately determining gold and silver, if necessary.

Number on the scale. 100ths mm.	Weight of gold button. mg.	Weight of silver button. mg.	Volume of the button. cu. mm.	Number on the scale. 100ths mm.	Weight of gold button. mg.	Weight of silver button. mg.	Volume of the button. cu. mm.
2	0.0001	0.00004	0.000004	42	0.747	0.406	0.0388
3	0.0003	0.00015	0.000014	43	0.802	0.436	0.0416
4	0.0006	0.00035	0.000034	44	0.859	0.467	0.0446
5	0.0013	0.00069	0.000065	45	0.919	0.500	0.0477
6	0.0022	0.0012	0.00011	46	0.982	0.534	0.0510
7	0.0035	0.0019	0.00018	47	1.047	0.569	0.0544
8	0.0052	0.0028	0.00027	48	1.115	0.606	0.0579
9	0.0074	0.0040	0.00038	49	1.186	0.645	0.0616
10	0.0101	0.0055	0.00052	50	1.261	0.686	0.0655
11	0.0134	0.0073	0.00070	51	1.338	0.727	0.0695
12	0.0174	0.0095	0.00091	52	1.418	0.771	0.0736
13	0.0222	0.0121	0.00115	53	1.501	0.816	0.0780
14	0.0277	0.0151	0.00144	54	1.588	0.863	0.0824
15	0.0340	0.0185	0.00177	55	1.678	0.912	0.0871
16	0.0413	0.0225	0.00214	65	1.771	0.963	0.0920
17	0.0495	0.0269	0.00257	57	1.867	1.016	0.0970
18	0.0588	0.0320	0.00305	58	1.967	1.070	0.1022
19	0.0692	0.0376	0.00359	59	2.07	1.126	0.1075
20	0.0807	0.0439	0.00419	60	2.18	1.185	0.1131
21	0.0934	0.0508	0.00485	61	2.29	1.245	0.1189
22	0.107	0.0584	0.00558	62	2.40	1.307	0.1248
23	0.123	0.0667	0.00637	63	2.52	1.371	0.1309
24	0.139	0.0758	0.00724	64	2.64	1.438	0.1373
25	0.158	0.0857	0.00818	65	2.77	1.506	0.1438
26	0.177	0.0963	0.00920	66	2.90	1.577	0.1505
27	0.199	0.108	0.0103	67	3.03	1 649	0.1575
28	0.221	0.120	0.0115	68	3.17	1.724	0.1646
29	0.246	0.134	0.0128	69	3.31	1.802	0.1720
30	0.272	0.148	0.0141	70	3.46	1.881	0.1796
31	0.300	0.163	0.0156	71	3.61	1.963	0.1874
32	0.330	0.180	0.0172	72	3.76	2.047	0.1954
33	0.362	0.197	0.0188	73	3.92	2.133	0.2037
34	0.396	0.216	0.0206	74	4.09	2.222	0.2122
35	0.432	0.235	0.0225	75	4.25	2.313	0.2209
36	0.470	0.256	0.0244	76	4.43	2.407	0.2298
37	0.511	0.278	0.0265	77	4.60	2.504	0.2390
38	0.553	0.301	0.0287	78	4.78	2.602	0.2485
39	0.598	0.325	0.0311	79	4.97	2.704	0.2582
40	0.645	0.351	0.0335	80	5.16	2.81	0.268
41	0.695	0.378	0.0361	81	5.36	2.91	0.278

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.	Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
100ths mm.	mg.	mg.	cu. mm.	100ths. mm.	mg.	mg.	cu. mm.
82	5.56	3.02	0.289	92	7.85	4.27	0.408
83	5.77	3.14	0.299	93	8.11	4.41	0.421
84	5.98	3.25	0.310	94	8.38	4.55	0.435
85	6.19	3.37	0.322	95	8.65	4.70	0.449
86	6.41	3.49	0.333	96	8.92	4.85	0.463
87	6.64	3.61	0.345	97	9.20	5.00	0.478
88	6.87	3.74	0.357	98	9.49	5.16	0.493
89	7.11	3.87	0.369	99	9.78	5.32	0.508
90	7.35	4.00	0.382	100	10.08	5.48	0.524
91	7.60	4.13	0.395				

SPECIFIC GRAVITY OF GOLD-SILVER ALLOYS.

Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.
0	19.258	34	14.984	68	12.263
1	19.099	35	14.887	69	12.198
2	18.940	36	14.791	70	12.133
3	18.785	37	14.697	71	12.069
4	18.632	38	14.603	72	12.007
5	18.483	39	14.511	73	11.944
6	18.335	40	14.420	74	11.882
7	18.190	41	14.330	75	11.821
8	18.047	42	14.241	76	11.761
9	17.906	43	14.153	77	11.700
10	17.767	44	14.066	78	11.641
11	17.631	45	13.980	79	11.582
12	17.497	46	13.896	80	11.525
13	17.364	47	13.813 ·	81	11.467
14	17.234	48	13.730	82	11.410
15	17.106	49	13.648	83	11.353
16	16.979	50	13.568	84	11.297
17	16.855	51	13.488	85	11.242
18	16.731	52	13.409	86	11.187
19	16.610	53	13.331	87	11.133
20	16.491	54	13.254	88	11.079
21	16.374	55	13.178	89	11.026
22	16.258	56	13.103	90	10.973
23	16.144	57	13.029	91	10.921
24	16.031	58	12.955	92	10.871
25	15.920	59	12.882	93	10.819
26	15.810	60	12.811	94	10.768
27	15.702	61	12.739	95	10.718
28	15.595	62	12.669	96	10.658
29	15.490	63	12.600	97	10.619
30	15.386	64	12.531	98	10.570
31	15.283	65	12.463	99	10.521
32	15.183	66	12.395	100	10.473
33	15.083	67	12.329		

NOTES ON SOME BLOWPIPE TESTS.

BY JOSEPH W. RICHARDS..

Closed Tube Test.—This test may easily be made quantitative for approximate determinations of water, volatile sulphur, etc. A weighed amount of material is put into the tube, tapped down, and heated regularly. The upper part of the tube containing the sublimate is then nicked with a file and broken off. If water is being determined, two small corks are put into its ends, to prevent evaporation. The piece of tube and sublimate are then weighed ; then the tube is heated until the sublimate is driven off, and weighed again. The results on pyritic ores have proved satisfactory. A piece of göthite gave ·10.28 per cent. water ; theory requires 10.11 per cent. Time, five minutes.

Open Tube Test.—The behavior of the antimony coat is sometimes different from that usually described in the books. The entirely volatile oxide, Sb_2O_3, is sometimes the only product, not a trace of the non-volatile Sb_2O_4 being formed. I have observed this in allemontite, dyscrasite, and ullmannite, particularly. It takes nearly a red heat to volatilize this coating, and if the upper end of the tube from which the vapors are escaping be held in the flame, the latter is colored pale yellowish green (arsenic, pale blue). Penfield is the only writer who mentions the formation of this volatile coating exclusively by some minerals, but his experience as to which give it does not exactly coincide with mine.

It is important when testing in the open tube, if any substance whatever does not give a sublimate in lump, to powder it, and finally to heat with the blowpipe flame from the outside as hot as the glass will stand. Some sulphides, such as sphalerite and argentite, do not roast until thus heated. With these precautions, the test is uniformly reliable.

Flame Tests.—When testing for phosphoric acid, the assay on platinum wire is touched when *hot* to concentrated sulphuric acid, and brought into the outside edge of the Bunsen flame as *low down* as possible, and as slowly as possible. By thus proceeding, phosphorus can be infallibly detected in any combination, according to my experience, thus rendering unnecessary the ammonium molybdate test. The flame is slightly bluish green close to the

wire, grayish green a short distance away, and yellowish green farther off.

When testing similarly for boron, the assay should be held slightly higher, say an inch higher, in a hotter part of the flame. When testing for boron with Turner's mixture, it is an advantage to moisten the mass to a paste with a drop of concentrated sulphuric acid, and then put moist into the edge of the flame.

Reduction to Metal.—When reducing with soda on charcoal, if an assay proves very refractory, it is uniformly of advantage, and never deleterious, to add some borax to the assay. This is particularly useful in reducing tin oxide, and is to be preferred to potassium cyanide because of its harmlessness.

Test for Fluorine.—The fusion with potassium bisulphate decomposes any fluoride, but the test of the vapors with Brazil wood paper is not reliable. Light, air, and age, seem to deteriorate rapidly the sensitiveness of the paper. I have found it more reliable to make the fusion in a rather large closed tube, of say 5 to 8 mm. diameter, heating regularly with the tube almost horizontal. The silica ring deposits just above the assay, and the odor of the gas is often quite plain. Cool the tube, nick it below the silica ring, break, and hold the upper end vertically under, and close to the nose. At this instant the odor of hydrofluoric acid will be perceived with certainty, if any has been driven off, and by a little experience the odor can be distinguished with as much certainty as the smell of ammonia. A still more conclusive proof consists in letting water run slowly over the silica ring. If it is merely a sublimate of a volatile salt, it will be dissolved and disappear; if it is the true silica ring, it will become gelatinous, seen under the lens, and on carefully drying the tube the white ring is again strongly in evidence.

Test for Arsenates.—All give the arsenic odor and coat on charcoal, but sometimes so slowly as easily to escape detection. Mixing with charcoal dust and soda, and fusing in the closed tube or open tube does not invariably give metallic arsenic or the oxide, on account of the heat being insufficient to reduce some arsenates, *e. g.*, of zinc. Putting this mixture in the lower end of an open tube, and playing on it with the reducing flame of the blowpipe directed into the tube, will always give the arsenic coating. All mercury compounds are also thus reduced, and deposit a mercury coating, and it is a good means of testing for antimonates, tellu-

rates and selenates, while ammonium compounds give ammonia gas.

Test for Silica in the S. Ph. Bead.—Many silicates are attacked rapidly, the bases dissolved, and the silica left either in flocks or as a skeleton. However, on long blowing, some silica dissolves in the bead, and if only a small piece of mineral is used and the blowing is strong, all may dissolve up clear. Hirschwald determined that the bead can dissolve 2.5 per cent. of its weight of silica ; my tests have shown close to 2 per cent. but that more can be dissolved if other bases are present. For instance, the bead dissolves—

2.25 per cent. of silica if no other base is present,
2.25   "   "   "   "   3.85 per cent. of alumina is present,
3.03   "   "   "   "   8.52   "   " lime   "   "
3.40   "   "   "   "   3.17   "   "   "   "   "
4.04   "   "   "   " 10.91   "   " zinc oxide is present.

It results from this behavior, that in silicates rich in bases, an amount of mineral equal to even 30 per cent. of the weight of the bead (as in thaumasite) may be dissolved up clear. Two observations will obviate this difficulty. If the mineral is not white, as it is attacked, the edges will become white and clear as it is being dissolved, and the presence of silica thus proved. If the piece is white or clear, the blowing must be interrupted several times, and then with the lens the silica can be recognized floating in the bead. If the bead is clear, a further addition of a lump, say one-third the size of the bead, will always, on further blowing, cause the opalescent milkiness due to silica. By attending to these points, I think that silica can be found with certainty in all these silicates which are easily decomposed.

A different case is presented by those silicates which are attacked slowly and dissolve *en masse*, without showing a skeleton. They are not numerous, and are principally the silicates of aluminum, glucinum, or zirconium. In such cases, by long blowing (five minutes), enough silica is usually dissolved in a small bead to make it milky opalescent, which silica alone produces when present in such a small amount as even less than three per cent. The presence of silica can thus be proved. The minerals which dissolve slowly in salt of phosphorus and do not contain silica are principally corundum, diaspore, chrysoberyl, cassiterite, spinel, chromite, gahnite, and xenotime. They should be brought to mind and kept in consideration in connection with such few silicates as dissolve very slowly like the above. '

NOTES ON SUGAR BEETS.

By P. F. Trowbridge.

OBTAINING THE TARE.

AT the different beet-sugar factories in Michigan, two methods are used for finding the amount of tare (dirt adhering to the beets).

1. A half bushel of beets is taken from each wagon or car, as a sample, satisfactory to both the farmer and the factory representative. From this sample 20 or 25 pounds are carefully weighed. These beets are then well brushed with bristle brushes, and retopped if the whole of the crown has not been removed. The beets are again weighed and the loss in weight computed to per cent. is reported as the amount of tare.

2. The weighed sample is washed in a revolving washer, allowed to drain for a few minutes, retopped if necessary and again weighed. The loss in weight is reported in terms per cent. The second method requires less labor and is more rapid. It is also more nearly in accord with the factory operation. The first method fails to remove every particle of dirt, but does remove many small rootlets and a small amount of the outside of the beets, especially if they have been frozen.

In method 2, the adherent water tends to decrease the amount of tare. In the following series of experiments made at one of the Michigan factories, care was exercised to make both samples from each load as representative as possible.

No. of sample.	Tare by method 1. Per cent.	Tare by method 2. Per cent.	Difference.
1	8.75	6.25	+2.50
2	10.00	8.75	+1.25
3	13.75	13.75	0.00
4	7.50	7.50	0.00
5	5.00	6.25	—1.25
6	21.25	22.50	—1.25
7	8.75	6.25	+2.50
8	10.00	7.50	+2.50
9	11.25	11.25	0.00
Average	10.14	10.00	—0.14

A further advantage of the second method is that frozen beets may be tared at once using warm water in the washer.

ANALYSIS OF THE SAMPLE.

The percentage of sugar in the beet is determined, in all the Michigan factories, by the indirect method of juice analysis, using a factor to express the results in terms of per cent. in the beets. A brief résumé of the methods employed may be of interest.

A portion of the tared sample (usually longitudinal quarters of six or eight beets) is pulped in a revolving grater. The pulped sample is mixed, pressed in a lever press, and the juice sent to the chemist for analysis. Factory methods vary somewhat at this point: (1) The sample is allowed to stand for fifteen or twenty minutes to allow the air bubbles to escape, after which the Brix reading is taken with correction for temperature; then 100 cc. of the sample are poured into a double graduated flask (100–110 cc.), and 10 cc. of basic lead acetate solution added. If foam renders filling to the mark difficult, a drop of ether or alcohol is used. The sample is thoroughly mixed, filtered through a dry filter and polarized. The per cent. of sugar in the juice is given in Schmitz's tables, and the factor adopted by the factory is used to express the results in terms of per cent. sugar in the beet. (2) After the Brix reading a double normal sample (52.1 grams) is measured with a sucrose pipette, which has a graduation on the stem indicating the amount to be taken for the different degrees Brix. The pipettes have been graduated with a pure sugar solution, and are not strictly accurate for beet juices, but the error is well within the range allowed by commercial methods. The sample is transferred to a graduated flask, 100 or 200 cc., 6 or 8 cc. of lead acetate solution added, the flask filled to the mark, and the sample mixed, filtered, and polarized. If 100 cc. flasks are used, one-half the reading gives the per cent. sugar in juice, and the factor gives per cent. in beet. (3) A double normal sample of the juice is weighed on a balance sensitive to 10 mg.; then proceed as in (2). All the methods give results, the commercial accuracy of which cannot be questioned. Method (1) by employing a larger sample reduces the errors of manipulation and reading, and is thus preferred by the writer.

THE FACTOR TO SHOW THE RELATION BETWEEN SUGAR IN JUICE TO SUGAR IN BEET.

The true factor to represent the relation of sugar in juice to

sugar in beet has been the subject of some controversy and hard feeling between the farmers and the factory managers. During the campaign of a year ago some of the Michigan factories used the factor 0.95, others as low a factor as 0.90, and it was claimed that one factory used a factor of 0.87. The factor 0.95 was formerly employed by the German chemists and was based on the fact that the marc in the beet is usually not far from 5 per cent. Scheibler's method of direct beet analysis showed the error of this assumption, and has brought about the abandonment of this factor on the continent.[1] During the fall and winter of 1899 the writer made a series of twenty-five analyses (method of operation given below) to determine this factor and found as an average 0.919, with a maximum of 0.956, and a minimum of 0.875. The table of results as given below is arranged not in order of the analyses but in order of the value of the factor.

No. of sample.	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.
1	14.6	12.8	0.875
2	15.4	13.6	0.880
3	15.1	13.3	0.881
4	16.0	14.2	0.888
5	15.2	13.5	0.888
6	14.1	12.7	0.899
7	14.8	13.6	0.902
8	15.5	14.0	0.903
9	16.9	15.4	0.911
10	15.3	14.0	0.915
11	15.3	14.0	0.915
12	14.4	13.2	0.917
13	16.8	15.4	0.917
14	16.8	15.4	0.917
15	16.7	15.4	0.922
16	15.7	14.5	0.924
17	15.1	14.0	0.927
18	15.6	14.5	0.929
19	15.1	14.1	0.934
20	11.4	10.7	0.938
21	15.3	14.4	0.941
22	15.7	15.0	0.955
23	15.4	14.7	0.955
24	15.8	15.1	0.956
25	15.8	15.1	0.956
Average	15.4	14.1	0.919

[1] Stohmann : "*Zucker Fabrikation*," (1900), 4te Aufl., p. 52.

METHOD OF ANALYSIS IN DETERMINING FACTOR.

The finely pulped samples are well mixed and duplicate samples are weighed for determination of sugar in beet by the hot alcohol digestion method. The remainder of the pulp is pressed in a lever press, and the juice analyzed by the methods previously described. The samples of pulp, 52.1 grams, are transferred to a 201.2 cc. flask, 6 to 8 cc. of basic lead acetate solution are added, and the flask is then filled three-fourths full of 90 per cent. alcohol. After the flask is fitted with a condenser tube it is heated, immersed in a water-bath, for thirty minutes. Care must be taken that the alcohol does not boil so violently as to force the pulp and juice into the condenser tube. The condenser tube and the neck of the flask are then rinsed with alcohol, and the flask filled nearly to the mark, the flask being turned from side to side to insure the removal of all air bubbles. The flask is then returned to the water-bath for three or four minutes, or until the alcohol is heated nearly to boiling. The contents of the flask are then cooled to about 17.5°. The flask is filled to the mark, thoroughly shaken, and the contents filtered through a dry filter, and polarized. In the filtering, the funnel must be covered to prevent evaporation of the alcohol, and the temperature of the room must be as nearly 17.5° as possible.[1] The reading of the polariscope gives the per cent. of sugar in the beet direct. The sugar in the juice divided by the sugar in the beet gives the factor.

During the campaign of a year ago, shortly after the writer had made the analyses reported above, Mr. E. E. Ewell, first assistant chemist of the Department of Agriculture, was called into the state to examine the working of one of the beet-sugar factories, and made eight analyses to determine the factor. He reported[2] an average factor of 0.9275, maximum 0.945, minimum 0.902.

During the present campaign the Holland Sugar Co., of Holland, Michigan, saves a handful of pulp from every sample analyzed, and for every ten samples this pulp is mixed and analyzed by hot water digestion. This establishes a factor for every ten samples. During three weeks in October they reported to the writer the finding of average factors of 0.91, 0.913, and 0.912.

The writer has made a number of analyses of beets grown the past season in a further study of this problem, with the following

[1] See Wiley: This Journal, 21, 568 (1899).
[2] House Document, No. 699, p. 146.

results: Average factor 0.917, minimum 0.883, maximum 0.955.

Number.	Purity	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.
1...................	81.4	13.6	12.2	0.897
2...................	80.2	13.5	12.5	0.926
3...................	78.2	13.4	12.8	0.955
4...................	80.4	11.5	10.4	0.904
5...................	78.0	12.5	11.7	0.936
6...................	83.1	13.0	11.6	0.892
7...................	84.7	15.0	13.8	0.920
8...................	84.5	14.6	12.9	0.883
9...................	77.7	11.0	10.1	0.918
10...................	77.1	11.1	10.4	0.937
Average	80.5	12.9	11.8	0.917

Mr. Ewell,[1] in his report, calls attention to reasons why there should be so great variations in the relation existing between the sugar in the juice and that in the beet as a whole. It is quite evident that the *average* factor expressing this relation lies between 0.91 and 0.92. If any one grower of beets has a large number of loads to deliver and thus obtains the average of many analyses the use of an average factor will not work injustice to either party. On the other hand the average of a few samples only, may work an injustice to the grower or to the factory.

Owing to the great number of analyses made daily at the factories (100 to 300), the chemists are forced to use the indirect method of juice analysis. The hot alcohol digestion method is too slow and also too expensive. The hot water digestion method, although more rapid than the hot alcohol digestion, is yet too slow for factory use under present factory conveniences. The instantaneous diffusion method of Pellet[2] can be made rapid enough for factory work, but so far as I am aware, it has not yet superseded the indirect method in any of the sugar factories in this country. Difficulty is experienced in pulping the beets sufficiently fine to insure accuracy of results. Theoretically every cell wall should be broken. The sugar does not diffuse through the cell walls with cold water until after the cell walls have been heated.[3]

THE MARC AND THE FACTOR.

It has been shown that the old factor 0.95, based on the approximate 5 per cent. of marc, has no justification. A few actual

[1] *Loc. cit.*
[2] Spencer : " Handbook for Beet-Sugar Chemists," p. 181 (1897).
[3] Stohman : *Loc. cit.*, p. 110.

determinations of marc and factor in the same sample will be of interest. The marc (insoluble fiber) determinations were made as directed by Fruehling and Schulz.[1]

Number.	Marc. Per cent.	Sugar in juice. Per cent.	Sugar in beet. Per cent.	Factor.	Factor on basis of marc.
1 · · · · · · · · · · · · · · ·	4.47	13.58	12.17	0.896	0.9553
2 · · · · · · · · · · · · · · ·	4.53	13.48	12.53	0.930	0.9547
3 · · · · · · · · · · · · · · ·	4.14	11.43	10.66	0.933	0.9586
4[2] · · · · · · · · · · · · · · ·	5.20	14.4	11.3	0.785	0.9480
5[3] · · · · · · · · · · · · · · ·	4.42	14.2	10.3	0.725	0.9558

VARIATIONS OF SUGAR CONTENT IN BEETS GROWN UNDER APPARENTLY UNIFORM CONDITIONS.

Complaint has been made at different factories in the state that two loads of beets drawn from the same field, and often from the same pit, would vary several per cent. in sugar content. At Marine City this year an average sugar content for about 60 acres of beets for one man was 14 per cent., yet from the same field one load gave 11.8 per cent. and another 18 per cent. This variation is in part due to the variable factor as discussed in the section above, and also in the variation in the sugar content in beets grown under apparently uniform conditions.

The writer raised a small patch of beets last season, about 25 by 50 feet, planting them in rows 16 inches apart, and thinning to about 9 inches in the row. From the patch 120 beets were selected that were of good form and size. Each of these beets were analyzed separately for sugar content some six weeks after they had been pulled. The average sugar content was 12.61 per cent; the lowest was 8.7 per cent., and the highest 18.2 per cent.

Of these 120 beets:

```
 1 beet contained between  8 and  9 per cent. sugar (8.7).
 1   "        "         "   9  "  10   "      "
14   "        "         "  10  "  11   "      "
22   "        "         "  11  "  12   "      "
39   "        "         "  12  "  13   "      "
19   "        "         "  13  "  14   "      "
18   "        "         "  14  "  15   "      "
 4   "        "         "  15  "  16   "      "
 1   "        "         "  16  "  17   "      "
 0   "        "         "  17  "  18   "      "
 1   "        "         "  18  "  19   "      "  (18.2).
```

[1] "Anleitung," 5th edition, p. 185.
[2] Sample No. 4 consisted of a very large hollow beet, but not decayed.
[3] Sample No. 5 consisted of three green beets.

It is surprising that beets grown under apparently uniform conditions of soil and culture should show such a range of sugar content. The variation of sugar content in individual beets shows the necessity of taking similar portions of several beets for the sample rather than the whole of one or two beets.

The purity (percentage of sugar in total solids) in ten samples from the same patch of beets averaged 80.5 per cent. and ranged from 77.1 to 84.7, as shown in the table on page 220.

COMPARISON OF ANALYSES BY DIGESTION WITH HOT ALCOHOL AND HOT WATER.

The German chemists have adopted the digestion with hot alcohol as the standard, while the French chemists rely upon the digestion with hot water. It will be of interest to compare the results of the two methods. The samples of beets were all grated on a hand vegetable grater, thoroughly mixed, and double normal samples weighed for analysis. The time of digestion was one-half hour in all cases. The general plan of manipulation as given in Fruehling and Schulz[1] was followed. Duplicate samples were taken in every case, three readings being made for each sample. The per cent. reported in the following table is the average of the six readings.

No. of sample.	Alcohol digestion. Per cent. sugar.	Water digestion. Per cent. sugar.	Difference. Per cent.
1	12.50	12.30	—0.2
2	12.65	12.59	—0.06
3	13.30	13.20	—0.1
4	11.90	11.73	—0.17
5	15.48	15.28	—0.20
6	16.00	15.79	—0.21
7	15.06	14.66	—0.4
8	11.81	11.81	0.00
9	13.23	13.44	+0.21
10	12.70	13.05	+0.35
11	13.10	13.02	—0.08
12	12.29	12.72	+0.43
13	13.54	13.24	—0.3
14	13.20	13.11	—0.09
15	11.86	12.19	+0.33
16	12.63	12.96	+0.33
17	13.88	13.64	—0.28
18	13.98	13.98	0.00
19	16.68	16.53	—0.15
Average	13.41	13.43	—0.02

[1] *Loc. cit.*, pp. 180 and 182.

The average of error between the two methods is scarcely greater in any case than would be likely to occur in ordinary duplicate analyses. Certainly the above results do not indicate that 0.2 per cent. should be deducted from all hot water digestions to give the correct data, as was maintained to the writer last winter by a German sugar chemist.

THE RICHEST PORTION OF THE BEET.

In answer to many inquiries some analyses were made tending to show what portion of the beet has the greatest sugar content. The samples were all carefully topped at the leaf line, thoroughly brushed and divided horizontally into approximately three equal portions. The samples were grated by hand, carefully mixed and analyzed by the hot water digestion method. The results are given in the following table :

No. of sample.	Upper portion of beet. Per cent. sugar.	Middle portion of beet. Per cent. sugar.	Lower portion. of beet. Per cent. sugar.
1	11.20	13.20	13.50
2	11.60	12.30	11.60
3	9.93	9.98	9.73
4	11.16	13.64	12.87
5	11.70	13.90	10.80
6	10.10	11.30	10.30
7	11.60	12.10	14.20
8	9.10	10.40	11.10
9	10.50	12.40	10.10
10	11.08	13.2	13.00
Average	10.9	12.2	11.7

Where only *portions* of beets are used to make up the sample for analysis, a full-length longitudinal section should be taken, and the same fractional portion of each beet.

ON THIOUREAAMIDINES : A CORRECTION.

BY HENRY L. WHEELER.

RECENTLY Wheeler and Sanders[1] published an article on ureaimido esters, thioureaimido esters, acylthioureaimido esters and ureaamidines. An examination of the behavior of the ureaimido esters towards organic bases showed that they reacted

[1] This Journal, 22, 365.

in every case. For example, phenylureaimidoisobutyl benzoate and aniline reacted as follows :

$$C_6H_5C\underset{OC_4H_9}{\overset{NCONHC_6H_5}{<}} + H_2NC_6H_5 =$$

$$C_6H_5C\underset{NHC_6H_5}{\overset{NCONHC_6H_5}{<}} + C_4H_9OH.$$
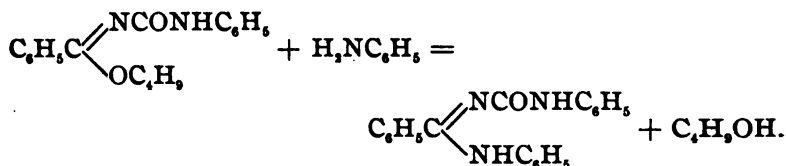
In other words this ureaimido ester behaved in the normal manner with aniline, and an amidine was formed, as was shown by analysis. That this is correct has now been thoroughly established by the preparation of the above ureaamidine from benzenyl-phenylamidine[1] and phenyl isocyanate.

When the corresponding thioureaimido esters and acylthiourea-imido esters were treated with aniline, β-naphthylamine, p-anisi-dine, etc., products were obtained which from analogy were assumed by the writer to be thioureaamidines, although in the five cases described the determinations of nitrogen invariably came low. It was at that time thought that these results were due to the fact that the compounds burn with great difficulty.[2]

After the above was published it was found that our analytical results agreed better with those calculated for the corresponding thiourea derivatives (column B, below) than with those of the supposed thioureaamidines (column A). The thiourea derivatives have now been prepared, and a comparison of these with our so-called thioureaamidines shows that the compounds are identical.

The following correction is therefore to be made in our work :

A.	B.
Benzenylphenylthiourea-p-anisylamidine	phenyl-p-anisylthiourea.
Benzenylphenylthioureaphenylamidine	diphenylthiourea.
Benzenylphenylthiourea-β-naphthylamidine	phenyl-β-naphthylthiourea.
Benzenylbenzoylthioureaphenylamidine	benzoylphenylthiourea.
Benzenylbenzoylthiourea-o-tolylamidine	benzoyl-o-tolylthiourea.

It has also been found that the true thioureaamidines are decidedly different from our previously described products. Two examples of these have been prepared by combining benzenylphenyl-amidine with phenyl mustard oil and benzoylrhodanide, respectively. The action of organic bases on the thioureaimido esters,

[1] Prepared by Pechmann's method : *Ber. d. chem. Ges.*, **30**, 1782 (1897).

[2] For an example of such a case, see benzoyl-*m*-chlorphenylurea and the correspond-ing thiourea. Wheeler and Johnson : *Am. Chem. J.*, **24**, 220 (1900).

therefore, proceeds as follows, giving a thiourea derivative and an **imido ester** or its reaction products :

$$C_6H_5C \Big\langle {}^{NCSNHC_6H_5}_{OC_2H_5} + H_2NC_6H_5 =$$

$$C_6H_5NHCSNHC_6H_5 + C_6H_5C(OC_2H_5) = NH.$$
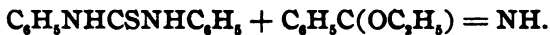
The reaction is unique inasmuch as it differs from that of both **oxygen analogues** and acylimido esters.[1] It may also be added that **phenylthioureaimidoisobutyl benzoate** gave **phenylthiourea** with **aqueous-alcoholic** ammonia ; and that **benzoylthiourea was obtained** from benzoylthioureaimidomethylphenyl acetate and **phenylhydrazine.**[2]

<div align="center">EXPERIMENTAL PART.</div>

Benzenylphenylureaphenylamidine, $C_6H_5C \Big\langle {}^{NCONHC_6H_5}_{NHC_6H_5}$, was **prepared** by dissolving 2 grams of benzenylphenylamidine in benzene **and** adding the calculated quantity of phenyl isocyanate (1.2 **grams**), whereupon the ureaamidine separated at once. It was **found** to be difficultly soluble in alcohol, more readily in benzene, **from which** solutions it separated in the form of fine needles melting **sharply** from 179°–180°. It was identical in appearance and **properties** with the product obtained from phenylureaimidoisobutyl **benzoate** and aniline.

Benzenylphenylthioureaphenylamidine, $C_6H_5C \Big\langle {}^{NCSNHC_6H_5}_{NHC_6H_5}$.—.

Two grams of benzenylphenylamidine and 1.3 grams of phenyl **mustard oil** were mixed, and fused on the water-bath. On warming **for a** few minutes, the mixture solidified. It was then crystallized from benzene, whereupon fine needles or prisms separated, **melting** at 138°. This material had neither the appearance nor **properties** of the substance previously described under this name. **A nitrogen** determination gave :

	Calculated for $C_{20}H_{17}N_3S$.	Found.
Nitrogen	12.68	12.60

Phenylthioureaimidoisobutyl Benzoate and Aniline gave a product **crystallizing** from alcohol in plates which melted at 151°–152°.[3]

1 Wheeler and Walden: *Am. Chem. J.*, **20**, 568, (1898).
2 *Loc. cit.*
3 *Loc. cit.*

A specimen of Kahlbaum's thiocarbanilide had the same appearance and properties, and when a portion was mixed with this material the melting-point was not altered.

Calculated for $C_6H_5C(NHC_6H_5)=NCSNHC_6H_5$. $C_{20}H_{17}N_3S$.	Calculated for $C_6H_5NHCSNHC_6H_5$. $C_{13}H_{12}N_2S$.	Found.
Nitrogen .. 12.6	12.2	12.0.

This material is therefore diphenylthiourea.

Phenylthioureaimidomethyl Benzoate and Paraanisidine gave a product which, when crystallized from alcohol and amyl acetate, melted at about 180°.[1] On mixing phenyl mustard oil and *p*-anisidine, the compounds combined with evolution of heat. When the white mass, thus formed, was crystallized from amyl acetate it melted at 170° ; on crystallizing then from alcohol it melted at about 180° and seemed to be identical in every respect with the compound previously obtained from the ureaimido ester and *p*-anisidine. An analysis of the substance obtained in the latter manner gave :

Calculated for $C_6H_5C(NHC_6H_4OCH_3)=NCSNHC_6H_5$. $C_{21}H_{19}ON_3S$.	Calculated for $C_6H_5NHCSNHC_6H_4OCH_3$. $C_{14}H_{14}ON_2S$.	Found.
Nitrogen 11.6	10.8	10.1

The substance is therefore phenyl-*p*-anisylthiourea, possibly mixed with some dianisylthiourea[2] which melts at 185° and contains 9.7 per cent. of nitrogen, and which may result on repeated crystallizations of the mixed thiourea.

Phenylthioureaimidoisobutyl Benzoate and β-Naphthylamine gave a compound which, when crystallized from alcohol and amyl acetate, formed minute plates, and melted, not sharply, at 182°–183°. This compound should be phenyl-β-naphthylthiourea, which, Mainzer[3] states, melts from 155°–157°, but which melts higher on repeated crystallizations, apparently undergoing decomposition. According to Freund and Wolf[4] it melts at 165°. I have found that when phenyl mustard oil and β-naphthylamine are mixed and the product crystallized once from amyl acetate it melts at 177°–182°. On boiling this product with alcohol it melted, not sharply, from 182°–183°, and agreed in all its properties with the material obtained from the thioureaimido ester and β-naphthylamine. When the two specimens were mixed no change in melt-

[1] *Loc. cit.*
[2] Salkowski : *Ber. d. chem. Ges.*, **7**, 1012 (1874).
[3] *Ber. d. chem. Ges.*, **15**, 1417 (1882).
[4] *Ber. d. chem. Ges.*, **25**, 1468 (1892).

ing-point was observed. The result of our previous analysis follows :

	Calculated for $C_6H_5C(NHC_{10}H_7)=NCSNHC_6H_5.$ $C_{24}H_{19}N_3S.$	Calculated for $C_6H_5NHCSNHC_{10}H_7.$ $C_{17}H_{14}N_2S.$	Found.
Nitrogen	11.0	10.0	10.0

This material is therefore phenyl-β-naphthylthiourea.

Benzoylthioureaimidoisobutyl Benzoate and Aniline gave a product melting from 145°–146°. This is identical with benzoylphenylthiourea described by Miquel,[1] as melting at 148°–149°. Our previous analysis is appended :

	Calculated for $C_6H_5C(NHC_6H_5)=NCSNHCOC_6H_5.$ $C_{21}H_{17}ON_3S.$	Calculated for $C_6H_5NHCSNHCOC_6H_5.$ $C_{14}H_{12}ON_2S.$	Found.
Nitrogen	11.6	10.9	11.2

When benzenylphenylamidine was mixed, either dry or in benzene solution, with benzoylrhodanide, a small amount of well crystallized material, melting at about 162° was obtained, in addition to some varnish. As the properties of these products had nothing in common with those of the above compound, the mixture was not further examined.

Benzoylthioureaimidoisobutyl Benzoate and o-Toluidine were stated to react, giving a product melting from 116°–117°. The same product has now been prepared from benzoylrhodanide and orthotoluidine, which, as Dixon[2] states, melts at 118–119°. On mixing this with our material the melting-point was not altered. Our former analysis is annexed :

	Calculated for $C_6H_5C(NHC_6H_4CH_3)=NCSNHCOC_6H_5.$ $C_{22}H_{19}ON_3S.$	Calculated for $C_6H_5CONHCSNHC_6H_4CH_3.$ $C_{15}H_{14}ON_2S.$	Found.
Nitrogen	11.2	10.3	10.8

NEW HAVEN, CONNECTICUT,
February 8, 1901.

A SPECIAL CRUCIBLE FOR CARBON COMBUSTIONS.

BY PORTER W. SHIMER.

IT may, perhaps, be remembered that in a former paper by the writer on "Carbon Combustions in a Platinum Crucible,"[3] the crucible was cooled externally by means of wet wick in contact with its upper part, drawing its supply of water from a circular trough kept full by the overflow from a hollow stopper.

[1] *Ann. Chem.* (Liebig), [5], **11**, 313.

[2] *J. Chem. Soc.* (London), **55**, 622.

[3] This Journal, **21**, 557, July, 1899.

By this arrangement witn wet wick and water-cooled stopper, it
is possible to use an ordinary platinum crucible for carbon com-
bustions and other work in which it is necessary to heat sub-
stances to high temperatures in special atmospheres.   While wet-
wick is effective, it is somewhat troublesome and needs a little
attention.   To displace the wick and trough, I have devised a
special crucible provided, in its upper part, with a platinum cool-
ing chamber about ½ inch wide and ¼ inch deep, having short
platinum inlet and outlet tubes at opposite sides.   The water,
after flowing through the stopper, is conducted to the cooling
chamber of the crucible by bent glass and rubber tubing, through
which it flows to waste.

The rubber band, by which the crucible is tightly closed, is
thus effectually cooled on its inner side by contact with the cold
stopper, and on its outer side by contact with the cold top of the
crucible.   The lower part of the crucible may be heated to the
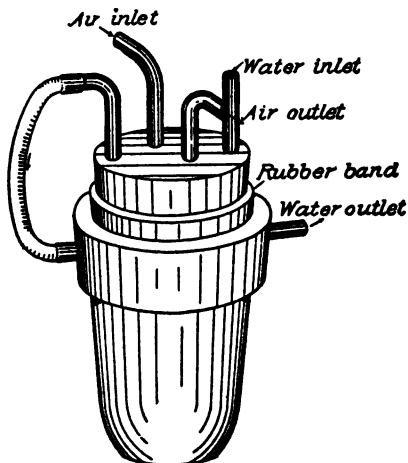
Fig 1.
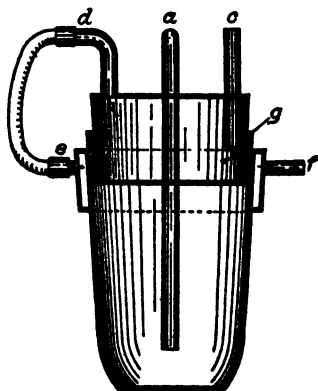
Fig 2.

full temperature of the blast-lamp without affecting the rubber
in the least.   In addition to the greater neatness and convenience
of this form of crucible, it also has the advantage of greater stiff-
ness by reason of the cooling chamber, and a smaller flame is
needed to bring the crucible to a red heat.   The flame of a
good Bunsen burner gives enough heat for the combustion in air
of carbon from steel.   For graphite and direct combustions, of

course, a blast-lamp is necessary. Direct combustions of difficultly soluble alloys may be made very readily in this crucible by mixing the finely divided alloy with lead chromate in a small porcelain crucible and placing the latter in the platinum crucible for combustion, as practised by Mr. C. A. Buck, of the Bethlehem Steel Co.

The construction of the crucible and stopper will be readily understood by reference to Figs. 1 and 2. The air or oxygen inlet is at a. The cold water enters the stopper at c, and leaves it at d, from which point it is led by means of a rubber tube to e, where it enters the platinum chamber surrounding the top of the crucible. The water runs to waste at f; or, the direction of the flow of water may be reversed, the water entering at f and escaping at c. The band of pure, black rubber, such as can be had at most stationers, is shown at g. It is essential that these bands be of the best quality of rubber obtainable, for such a band will make an absolutely tight joint with the crucible, and one band may be used for many combustions. Before inserting the stopper into the crucible, the band should be wetted with a little water, to lessen friction and secure a tight joint.

For the determination of combined water in ores, minerals, and cements, it may be mentioned here, the circulating water must be preheated to prevent condensation of the water driven out by the ignition of the sample on the cool stopper and upper part of the crucible.

THE COMPLETE ANALYSIS OF FEEDING MATERIALS.

BY C. A. BROWNE, JR., AND C. P. BEISTLE.

IN the ordinary analysis of feeding-stuffs it has been the general custom to determine only a few of the many constituents present ; for the computation of rations or for the determination of feeding values an estimation of the moisture, fat, protein, ash, and fiber is all that is usually required, the percentage of undetermined matter being simply designated "nitrogen-free extract."

This method of procedure, while sufficient for many purposes, is by no means scientifically accurate, and chemists have for a

long time felt that not only should a closer study be made of the various substances, or rather groups of substances, such as ether extract, protein, and fiber, but also that more attention should be given to that large group of undetermined bodies which make up the nitrogen-free extract.

Considerable work has been accomplished along these lines during the past few years, both in this country and abroad. Good workable methods have been adopted for the determination of sugars, starch, and pentosans, and some attempts have been made towards effecting a separation of the various lignin and cellulose bodies, which make up the greater part of what is termed crude fiber. In many cases, more particularly in the analysis of grains, the percentages of the various constituents will approximate very closely 100 per cent., but in other cases, as with feeds rich in fiber, such as hay and straw or even certain cereal products, a considerable discrepancy still exists.

In the spring of 1899 a sample of distillery waste or mash was received at the Penna. Experiment Station from the Heinz Pickle Co., of Pittsburg, Pa. A portion of the sample, which was very moist and had slightly fermented, was examined for alcohol, and fixed and volatile acids; the rest of the material was dried as quickly as possible, then ground, and subjected to the customary fodder analysis with the following results:

	Per cent.
Moisture	3.83
Crude fat	10.25
Crude fiber	17.73
Ash	1.82
Protein	23.44
Total	57.07
Nitrogen-free extract	42.93

A determination of starch in the material by the diastase method gave less than 3 per cent., showing that the malting process had been quite complete. A determination of the furfural-yielding compounds or pentosans gave about 25 per cent., showing the material to be very rich in these bodies as was to be expected from the concentration which other constituents of the mash would undergo, with the elimination of the starch. There still remained, however, some 15 per cent. of material unaccounted for. This appeared to us such an unusually large

amount for a cereal product, that we were led to make a more complete study of the undetermined residuum.

In the choice of a method applicable to a case of this kind, the writers were guided, to a great extent, by a scheme of analysis devised by H. C. Sherman.[1] The scheme adopted by us in the present instance is given herewith and differs from that of Sherman in but few respects. We have divided the lignin bodies into two classes,—the lignic acids which are removable directly by NaOH, and the lignin which is removable only after chlorination. While, as Sherman says, "there may be no established chemical difference on which to rest such a distinction," we believe that there is a physiological difference, in that the lignin which is removable only after chlorination is of a more condensed variety than that removed by direct treatment with NaOH. We have also introduced the step, since an opportunity was given of studying the solvent action exercised by the alkaline solution employed in ordinary crude-fiber analysis.

SCHEME FOR THE ANALYSIS OF DISTILLERY WASTE.

(Four samples of 5 grams each were taken for analysis.)

Per cent.

I. Samples were dried for 8 hours at 100°C............................. Loss = Moisture, 3.83

II. Residues from I extracted with anhydrous ether 16 hours...... Extract = Crude fat, 10.25

III. Residues from II boiled with 95 per cent. alcohol 30 minutes, cooled, made to 100 cc. with alcohol, filtered, and filtrates combined:

	Original substance. Per cent.	
a. Extract determined in aliquot	3.62	
b. Ash " " "	0.10	
c. Protein " " "	1.20	
d. Sugars " " " (by copper reduction)....	0.00	Sugar, 0.00
Undetermined matter [a − (b + c + d)]...........	2.32	

IV. Residues from III treated with water at laboratory temperature over night; made to 100 cc. with water, filtered, and filtrates combined.

[1] This Journal, 19, 291.

 e. Extract determined in aliquot   4.50

 f. Ash   "   "   "   0.46

 g. Protein   "   "   "   0.73

 h. Dextrin (?) "   "   "

 (by inversion and copper reduction)..............   2.13   Dextrin (?), 2.13

 Undetermined matter [*e* — (*f* + *g* + *h*)]...........   1.18

V. Residues from IV dried and weighed, then reground and the starch determined by the diastase method; residues dried and reweighed.

 i. Residue determined before diastase treatment·......   78.29

 j. Starch determined in extract from diastase treatment..   2.66   Starch, 2.66 (?)

 k. Residue determined after diastase treatment.........   73.87

VI. Residues from V boiled 30 minutes with 200 cc. H_2SO_4 1.25 per cent., filtered, washed with hot H_2O and alcohol, dried, weighed, and then combined.

 l. Residues determined after H_2SO_4 treatment 45.42

 m. Protein determined in aliquot of combined residues   16.56

 n. Ash determined in aliquot of combined residues.......   0.95

 o. Carbohydrates in residue [*l* — (*m* + *n*)]..........   27.91

VII. Aliquots from combined residues of VI boiled 30 minutes with 200 cc. NaOH 1.25 per cent., filtered, washed with hot H_2O and alcohol, dried, and weighed.

 p. Residue determined after NaOH treatment........   17.94

 q. Protein determined in aliquot of residue 0.63

 r. Ash determined in aliquot of residue 0.21

 s. Carbohydrates in residue [*p* — (*q* + *r*)] 17.10

 t. Carbohydrates removed by NaOH treatment (o — s)   10.81   Lignic acids, 10.81 (?)

VIII. Residues from VII chlorinated 1
hour, then boiled 5 minutes
with 2 per cent. Na_2SO_3 and 0.2
per cent. NaOH solution
(method of Cross and Bevan),
filtered, washed, with hot H_2O
and alcohol, dried, and
weighed.

    u. Residue determined after
chlorination process 16.26

    v. Protein determined in aliquot
of residue 0.19

    w. Ash determined in aliquot
of residue.............. 0.11

    x. Carbohydrates in residue
$[u - (v + w)]$ 15.96

    y. Carbohydrates removed by
chlorination process $(s - x)$ .... 1.14   Lignin, 1.14

    z. Pentosans in residue *u* 5.62
per cent., or of original
substance 0.91

    Cellulose $[u - (v + w + z)]$ 15.05   Cellulose, 15.05

Pentosans determined in original substance by phloro-
glucin method................................. Pentosans, 24.86

Nitrogen determined in original substance 3.75 per cent.,
$N \times 6.25$ = protein .... Protein, 23.44

Ash determined in original substance...... .... Ash, 1.84

                                                             ——

        Total... 96.01

The sum of the various ingredients in the above table amounts
to 96.01 per cent., thus leaving an undetermined residuum of
about 4 per cent. It was thought at first, that the undetermined
matter in the alcoholic and aqueous extracts might explain this
deficiency ; the sum of this undetermined matter in the above
scheme, it will be seen, amounts to 3.5 per cent., and if this be esti-
mated as resin or gum, as is sometimes done, there would remain
but about 0.5 per cent. of material unaccounted for.

Before working upon this assumption, however, it was thought
best to make further studies as regards the actions of the various
solutions employed in the above scheme. A second series of 4
samples were carried through exactly as the first with the addi-
tional determination of the pentosans in the residues after each
stage of the process. The following results were secured :

<div align="right">Per cent.</div>

   I. Pentosans in original material........................ 24.86
  II. Pentosans in residue after alcohol and water treatment.. 22.16
 III. Pentosans in residue after malt digestion.............. 20.98
 IV. Pentosans in residue after H_2SO_4 treatment............. 3.32
  V. Pentosans in residue after NaOH treatment............. 0.87

It appears from the above results that several per cent. of material of a pentose nature finds its way into either the alcoholic or aqueous extracts. Such substances, owing to their marked copper-reducing power, would naturally affect the sugar or dextrin determinations. Since no copper-reducing bodies were removed by the alcohol, the inference is, that the pentoses dissolved were removed entirely by the water. The writers believe that the copper-reducing power of the aqueous extract, as shown in the scheme, was due mostly or even entirely to bodies of a pentose nature, and that a serious error may thus exist in the process usually employed for determining dextrin in feeding materials.

The undetermined matter of the alcoholic extract is no doubt made up of some unclassified constituents, such as resin, etc., and at this stage of the analysis there is probably to be found a part of the discrepancy which sometimes exists in the complete analysis of feeding materials.

Another fact in connection with the pentosan determinations is that 1.18 per cent. of pentosans disappears during the malt digestion. To test this in another way, the pentosans were determined in the extract from the malt digestion. The following results were secured:

<div align="right">Per cent. of
original sub-
stance.</div>

Pentosans in extract from malt digestion................ 2.71
Pentosans in malt solution............................. 1.29

Difference equals pentosans actually removed........... 1.42

This figure coincides very closely with the value previously given, and proves unquestionably that the malt solution does exert some solvent action upon the pentosans. In order to determine how much the removal of pentosans was due to the solvent action of water alone, a blank experiment was run, using the same amount of water as malt solution, and conducting the digestion for the same length of time; the aqueous extract was then concentrated, and a determination of pentosans made in the

usual way ; the amount thus obtained amounted to 0.85 per cent. of the original material, thus showing that a considerable amount, but not all, of the pentosans removed during the malt digestion, was due simply to the solvent action of water.

A removal of pentosans during the diastase digestion introduces somewhat of an error into the starch determination.   Starch was present in the material analyzed, as was shown by the slight iodine reaction, but the percentage indicated in the scheme is undoubtedly too high.   The error thus introduced into the starch determination by the solubility of pentosans, would probably never be much greater than the above case, owing to the large amount of pentosans present and the long period of digestion, which, in the present instance, was twelve hours.

From the table of pentosan determinations, it is seen that 17.66 per cent. of pentosans disappears during the treatment with sulphuric acid.   The extract from this treatment was saved in order to make a comparative determination of the pentosans removed, by the copper reduction process.

The extract was diluted to 300 cc., after adding sufficient H_2SO_4 to make the total amount 2 per cent. of the solution after diluting, and the whole boiled for six hours in a 500 cc. flask connected with a condensing tube.   After cooling, the solution was neutralized with dilute NaOH, using phenolphthalein, and the volume completed to 500 cc.   25 cc of this solution gave a weight of reduced copper[1] equivalent to 21.65 per cent. dextrose, which would be equivalent to 21.00[2] per cent. pentoses, or 18.48[3] per cent. pentosans.

Another point which must not be overlooked in the complete analysis of feeding materials, is the presence of furfural-yielding constituents in the material left after the chlorination process. In the scheme, the writers have estimated these bodies as pentosans, and subtracted their percentage from the percentage of fiber after chlorination, in calculating the percentage of cellulose.   It may be, however, that these furfural-yielding constituents of the fiber, after chlorination, are of an oxycellulose nature, as appears from the work of Cross and Bevan, in which case the total percentage of pentosans would need to be corrected.

[1] Allihn's method of copper reduction was followed in this and all other instances.
[2] Dextrose × 0.97.   Stone : *Am. Chem. J.*, 13, 73.
[3] Pentoses × 0.88.

In conclusion, it may be said that, while the sum of the percentages of the different constituents in many feeding stuffs does not equal exactly 100 per cent., the results are as close as could be expected with the present methods of analysis. In addition to the uncertainties of some of the analytical steps just pointed out, it should also be noted that the factors used for the calculation of protein and pentosans are more or less of an arbitrary nature, and cannot be considered absolute in the case of any particular feeding material. In view of this, and our present incomplete knowledge of many of the various proximate constituents of feeding materials, the exactness attainable in some other departments of analytical chemistry is not at present to be hoped for.

CATALYSIS IN CONCENTRATED SOLUTIONS.

BY J. M. CRAFTS.

THE study of the catalytic action of acids in very dilute solutions has led to the discovery of a number of simple relations between ionic dissociation, chemical affinity, and electrical conductivity, and the conclusion is universally accepted that the active agent is the hydrogen ion. The ratio of the velocity of the reaction to the concentration of the catalysor is nearly constant in dilute solutions of strong acids, but when ionic dissociation is diminished by increasing concentration, or in the case of weak acids by the presence of bodies which reduce the concentration of hydrogen ions, the ratio of velocity to concentration diminishes ; a small acceleration has, however, been observed when certain salts are added to the solutions of strong acids. Most of the subjects for experiments, such as the decomposition of esters, the inversion of sugar, etc., do not admit of the employment of very concentrated acid solutions, because the catalysor would then enter into the reaction, forming by-products.

It seemed interesting to study the hydrolysis of the sulphonic acids by means of chlorhydric acid and other strong acids, because here the reaction is catalytic in the sense that it is induced by the presence of a strong acid which does not enter into the final products, nor does it even form intermediate products in the same evident way as in esterification by sulphuric acid, or in the oxidation of sulphurous acid through the medium of nitrous fumes, nor does the degree of concentration of the catalysing

agent change the nature of the products, which are only sulphuric acid and hydrocarbon.

The results given below show that the rapidity of the reaction instead of being proportional to the concentration of the catalysor, rises to a thirty-fivefold greater rapidity when 38 per cent. chlorhydric acid solution is employed instead of 19 per cent., and a very remarkable result was obtained by adding to a 38 per cent. chlorhydric acid solution one-half its weight of zinc chloride, the rapidity of the reaction being then raised more than threefold.

It is thus apparent that increased concentration and other influences which must be supposed to diminish ionic dissociation, promote to a high degree the rapidity of the hydrolytic action, and this fact would point to the inference that the hydrolysis is promoted by $HCl + H_2O$, and not by the hydrogen ions, unless some other predominant and preparatory reaction can be attributed to dehydrating agents like chlorhydric acid, sulphuric acid, and zinc chloride. The study of this hypothesis has been undertaken, but seems to demand an extended series of experiments before an opinion can be formed, and it is desired to give in this preliminary notice a description of experiments which establish a sharp distinction between catalysis in dilute and concentrated solutions. It is possible that the newly observed phenomena may be quite different from catalysis and may require another name, but the old one has been made to hide so many mysteries that it will serve to cover this one also, until a new theory of the reaction can be founded upon a larger number of experiments.

I will give the results of some 150 measurements in sealed tubes chiefly at 100°, and will leave aside a larger number of experiments which were made by passing steam through sulphuric acid solutions of sulphonic acids at different temperatures.

The work will be interrupted for a few months, and it is desired to reserve the field until the projects, which will be indicated for further experiments along the same line, can be executed and the data obtained for explanation, or at least for correct formulation of this interesting reaction.

EXPERIMENTAL RESULTS.

On heating in sealed tubes at 100°, the metaxylene-sulphonic acid (1 : 3 : 4) gives an easily measurable rate of decomposition

with chlorhydric acid of concentrations varying between 43 per cent. and 13 per cent. HCl gas ; and the intervals of time which it is necessary to heat in order to decompose 10 per cent. of the sulphonic acid, vary between thirty minutes and more than one hundred hours, according to the strength of the acid. Benzene and toluenesulphonic acids do not react at this temperature, paraxylenesulphonic acid acts very slowly, and the sulphonic acids of the higher homologues of benzene act too rapidly at 100°, and, moreover, these acids are only partly soluble in strong chlorhydric acid even at 100°. For these reasons the first series of determinations was made with the metaxylenesulphonic acid, $C_8H_9SO_3H + 2H_2O$. The crystals of the acid can be kept for any length of time exposed to the air with only slight hygroscopic changes of weight.

A mode of preparation, which was found much more advantageous than the passage by the barium salt, consists in using directly the solution obtained by heating, during two hours at 100°, 2 parts of common sulphuric acid and 1 part hydrocarbon. The immediate product is added cautiously, to prevent heating, to common chlorhydric acid (containing about 38 per cent. HCl) cooled to zero or below. Paratoluenesulphonic acid, the common forms of metaxylene and pseudocumene sulphonic acids, and the sulphonic acids of paraxylene and mesitylene are nearly insoluble in strong cold chlorhydric acid, and the fine crystalline precipitate can easily be washed with pure cold chlorhydric acid with little loss until entirely free from sulphuric acid. Exposure for two days on a glass plate suffices to remove all traces of chlorhydric acid, and to leave the pure sulphonic acids crystallized with their normal proportions of water of crystallization. The crystalline powder so obtained can be dissolved in water and recrystallized without change of weight. Paratoluenesulphonic acid has 1 molecule of water of crystallization ; the other acids named have 2 molecules. Paratoluenesulphonic acid so prepared melts at 102°; metaxylenesulphonic acid (1 : 3 : 4) at 59.8°; paraxylenesulphonic acid melts at 86°; pseudocumenesulphonic acid (1 : 3 : 4 : 5) at 112°.

The Hydrolysis, $C_8H_{10}SO_3 + H_2O = H_2SO_4 + C_8H_{10}$.—In each experiment a weighed quantity of the sulphonic acid was sealed with a weighed quantity of chlorhydric acid, or some other substance or acid as a catalysor, in a glass tube of about 1 cm.

diameter, which had been calibrated with weighed amounts of the hydrocarbons, xylene, cumene, etc.

The determinations were made, after heating a definite period, by measuring the height of the layer of hydrocarbon set free. Certain precautions were taken relative to the solubility of the hydrocarbon in the acid solution both hot and cold, and the time required for the complete separation of the dissolved hydrocarbon on cooling. A few control determinations of the sulphuric acid set free were also made, but in this preliminary notice it is not necessary to enter into the details of these operations, because even considerable errors of measurement and impurity of the sulphonic acids would not disguise the nature of the reaction, which it is designed to show.

A well determined and constant temperature was obtained by using the ebullition of pure substances, water and benzene, under atmospheric pressure. The tubes were always heated in contact with the liquid bath, and allowance was made for the time (about three minutes) required for a thermometer enclosed in a similar tube to take the temperatures of 79° or 99°. If the test is made by plunging the glass tube, containing a thermometer and filled with liquid, in a metal tube heated by boiling water to a constant temperature but only containing air, the transfer of heat through the air layer to the glass tube is so slow that nearly an hour is required for the thermometer to reach 100°.

A. Experiments with Metaxylenesulphonic Acid and Chlorhydric Acid.—In the following experiments (Nos I–XIII), the temperature was 99.7°–100°. The hours from the commencement of heating and the corresponding percentages of decomposition are given. The latter was usually determined by measuring the hydrocarbon set free in a tube which had been calibrated at the same place with known weights of the same hydrocarbon. It was usually necessary to wait some hours for the complete separation of the hydrocarbon which had dissolved at a high temperature in the acid liquid, but appeared to be almost completely separated in the cold, so that the readings became constant after intervals of an hour.

I. 10 grams metaxylenesulphonic acid, $C_6H_3CH_3(1)CH_3(3)SO_3H(4) + 2H_2O$, + 75 grams chlorhydric acid (10 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	0.0	136	8.7
32	2.2	156	8.7
64	4.3	172	9.4
104	5.6	212	10.0
120	6.5		

The apparent retardation of the decomposition during the first sixteen hours is probably only due to the solubility in the acid mixture of the first fraction of xylene, about 0.04 gram. If this is the case, about 1 per cent. should be added to all the measures.. The decomposition with a measurable rate of speed up to about 10 per cent., and from that point a decomposition of only 0.6 per cent. in forty hours, seems to indicate the presence of an impurity, possibly $C_6H_3CH_3$ (1) SO_3H (2) CH_3 (3), which decomposes more rapidly, while the pure acid, $C_6H_3CH_3$ (1) CH_3 (3) SO_3H (4), which remains is not decomposed by 10 per cent. chlorhydric acid solution.

II. Ten grams metaxylenesulphonic acid $+$ 75 grams chlorhydric acid (13.1 per cent. HCl). 0.43 gram xylene was added before heating in order to saturate the acid liquid, the height of the layer of xylene was noted after shaking, and was subtracted from subsequent readings.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	1.9	136	10.2
32	2.4	152	12.0
48	4.2	172	13.8
64	5.4	188	15.7
88	7.9	204	17.4
104	9.0	220	18.7
120	10.2		

The series was terminated by the breaking of the tube.

III. Ten grams metaxylenesulphonic acid $+$ 70 grams chlorhydric acid (19 per cent. HCl). No corrections were made for the solubility of xylene in the acid solution in this and in the subsequent experiments.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1.	144	40.5
20	6.4	160	44.6
24	9.0	176	47.8
40	14.7	192	51.1
56	20.0	208	54.8
72	21.7	224	58.1
88	25.7	240	61.0
104	30.7	256	63.8
128	36.4	272	66.3

IV. Ten grams metaxylenesulphonic acid + 30 grams chlorhydric acid (10.3 per cent. HCl) + 8.75 grams sulphuric acid.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1.0	96	31.8
8	2.5	112	36.2
12	4.0	133	40.8
16	7.0	155	46.3
32	12.6	175	51.9
48	17.6	191	55.4
64	23.1	231	63.9
80	27.7	279	70.4
		327	77.0

V. Ten grams metaxylenesulphonic acid + 93 grams chlorhydric acid (19 per cent. HCl) + 37.5 grams zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	3.0	24	30.9
8	13.4	28	31.1
12	16.0	32	34.8
16	22.0	36	38.8
20	26.0	40	42.3

VI. Twenty grams metaxylenesulphonic acid + 90 grams chlorhydric acid (25 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	3.6	52	55.2
8	10.0	56	58.0
12	16.0	60	60.9
16	20.3	64	64.8
20	27.1	68	67.7
24	32.0	72	69.8
28	35.6	88	77.7
32	39.2	104	84.1
36	44.9	120	86.9
40	46.3	136	90.1
44	48.1	152	91.5
48	52.0		

VII. Ten grams metaxylenesulphonic acid + 515 grams chlorhydric acid (25 per cent. HCl).

Hours.	Xylene. Per cent.
4	2
16	22
20	29

A large bulb with a narrow neck of very thick glass was used. The calibration of the somewhat conical neck was less exact, and the readings were more uncertain than in a tube.

VIII. Twenty grams metaxylenesulphonic acid + 70 grams chlorhydric acid (31.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	14.2	28	83.1
8	29.7	44	92.0
12	47.6	60	96.1
16	57.9	76	95.6
20	68.3	92	95.9
24	76.9		

IX. Ten grams metaxylenesulphonic acid + 550 grams chlorhydric acid (31.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	6.3	10	35.2
2	9.4	14	44.8
6	20.9	18	60.0

X. Twenty grams metaxylenesulphonic acid + 70 grams chlorhydric acid (38.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	34.9	48	91.8
8	67.7	64	93.0
12	83.7	80	94.5
16	88.7		

XI. Ten grams metaxylenesulphonic acid + 38 grams chlorhydric acid (38.4 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
$\frac{1}{2}$	0	$5\frac{1}{2}$	48.9
$\frac{1}{2}$	3	$6\frac{1}{2}$	56.5
$\frac{3}{4}$	5.7	$7\frac{1}{2}$	60.8
1	8.4	$8\frac{1}{2}$	66.6
$1\frac{1}{2}$	14.0	$9\frac{1}{2}$	70.6
2	18.6	$10\frac{1}{2}$	72.1
$2\frac{1}{2}$	23.5	$11\frac{1}{2}$	74.7
3	28.5	$13\frac{1}{4}$	79.7
4	37.2	$15\frac{1}{2}$	81.0
$4\frac{1}{2}$	41.0	$17\frac{1}{2}$	82.0

XII. Ten grams metaxylenesulphonic acid + 39 grams chlorhydric acid (43 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
2	38.2	9	90.7
4	68.6	10	91.0
5	77.2	14	92.8
6	86.0	18	94.2
7	89.5	22	97.3
8	90.4	38	97.7

XIII. Ten grams metaxylenesulphonic acid + 38 grams chlorhydric acid (38.4 per cent. HCl) + 19 grams ZnCl$_2$.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	28.1	6	92.2
2	55.0	10	96.4
3	75.9	14	97.5
4	86.1	18	99.8
5	90.3	.34	99.4

XIV. *Temperature 80.2°.*—Ten grams metaxylenesulphonic acid + 36 grams chlorhydric acid (38.4 per cent. HCl) + 18 grams zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	6.0	20	49.6
8	15.6	24	57.5
12	27.9	28	65.3
16	38.2	32	72.2

B. Experiments with Metaxylenesulphonic Acid Heated with Sulphuric Acid at 100°.—

XV. Ten grams metaxylenesulphonic acid + 35 grams dilute sulphuric acid (25 per cent. H$_2$SO$_4$) were heated twenty hours at 100°. There was no sign of separation of xylene.

XVI. Ten grams metaxylenesulphonic acid + 112 grams dilute sulphuric acid (50 per cent. H$_2$SO$_4$).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	4.2	56	69.6
8	13.9	60	71.4
12	21.2	64	74.4
16	27.8	68	76.3
20	34.5	72	78.1
24	40.6	76	79.3
28	44.2	80	81.7
32	47.8	96	85.4
36	52.7	112	86.0
40	56.3	128	87.2
44	59.3	144	88.4
48	64.2	160	88.4
52	66.6	176	88.4

XVII. Ten grams metaxylenesulphonic acid + dilute sulphuric acid (75 per cent. H$_2$SO$_4$).

Soon after heating, the well-known phenomenon took place between the diluted sulphuric acid and the sulphonic acid: a lighter layer of a viscous liquid rose to the top, and this was

covered by a smaller layer of xylene. The viscous layer which separated contained 5.5 per cent. of dissolved xylene, and the remainder had nearly the composition $H_2SO_4 + 2H_2O$ (33 per cent.) $+C_8 H_{10}SO_3 + 2H_2O$ (67 per cent.). It is more probable, however, that most of the water should be regarded as combined with sulphuric acid, and the greater part of the metaxylene-sulphonic acid must be anhydrous on account of its power of dissolving xylene. This view is confirmed by the fact that the crystalline hydrated sulphonic acid dissolves on gently warming in sulphuric acid, diluted with enough water to make 75 per cent. H_2SO_4 and then an acid separates later on heating, giving the upper viscous layer.

These experiments suggest the idea that all dehydrating agents may bring the crystalline hydrated sulphonic acids into an anhydrous state, and that the anhydrous form may exist in solution, and perhaps be more susceptible of hydrolysis than the hydrated acids. This hypothesis will be investigated.

C. Metaxylenesulphonic Acid Heated to 100° with Nitric Acid.—

XVIII. Ten grams metaxylenesulphonic acid + common nitric acid, diluted with an equal weight of water, were heated three hours at 100° in a sealed tube. There was no sign of xylene, and only traces of insoluble nitro derivatives. The pressure of gas due to oxidation was not very strong.

Thus nitric acid has no action favoring hydrolysis to be compared to that of a molecular equivalent of chlorhydric or sulphuric acid.

THE RELATION BETWEEN CONCENTRATION OF THE ACID SOLUTIONS AND THE RAPIDITY OF THE HYDROLYSIS.

Curves were plotted of all these series of experiments, and the following table gives the time required in each case to decompose 5, 10, 15, etc., per cent. of the sulphonic acids.

In experiments II to XVI the first vertical column of the above table gives the percentages by weight of HCl gas in the chlorhydric acid solution ; the second column gives the weights of acid solution to which in each case 10 grams of crystallized sulphonic acid were added, and the third vertical column gives for experiment IV a weight of H_2SO_4 added to the solution, while for experiments V, XIII, and XVI weights of $ZnCl_2$ were added.

The next 18 vertical columns give the hours and decimal frac-

PERCENTAGE DECOMPOSITION OF METAXYLENESULPHONIC ACID HEATED TO 100° WITH CHLORHYDRIC ACID.

	Percentage of chlorhydric acid.	Weight of liquid. Grams.	Added. Grams.	5 per cent.	10 per cent.	15 per cent.	20 per cent.	25 per cent.	30 per cent.	35 per cent.	40 per cent.	45 per cent.	50 per cent.	55 per cent.	60 per cent.	65 per cent.	70 per cent.	75 per cent.	80 per cent.	85 per cent.	90 per cent.	Velocity constant. Unit of time, 100 hours.
II.	13.0	75	......	55.0	118.0	182.5	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.089
III.	19.0	70	......	17.0	29.0	44.0	61.0	80.0	100.0	120.0	140.5	162.0	187.0	210.0	234.0	264.0	...	...	...	...	...	0.39
IV.	10.0	30	8.75 H_2SO_4	13.0	25.0	40.0	55.0	70.5	92.0	113.0	132.0	151.5	170.0	189.0	207.0	233.0	...	...	...	...	...	0.40
V.	19.0	93	37.5 $ZnCl_2$	4.5	6.5	10.0	14.0	18.5	24.0	30.0	37.5	...	...	...	...	...	...	...	...	...	...	...	1.43
VI.	25.0	45	......	5.0	8.0	11.0	14.5	18.5	23.0	28.0	33.5	39.0	45.5	52.0	58.5	65.5	73.5	84.0	92.0	...	...	1.59
VIII.	31.4	35	......	...	...	4.2	5.3	6.4	7.6	9.0	10.3	11.6	13.0	14.6	16.4	18.5	20.8	23.3	25.8	29.1	35.0	5.75
IX.	31.4	550	......	0.8	2.2	3.6	5.0	6.6	8.3	10.0	11.9	13.9	15.4	16.8	18.0	...	...	...	...	...	...	5.10
X.	38.4	35	......	...	...	...	...	...	...	4.0	4.5	5.0	5.5	6.1	6.8	7.5	8.5	9.5	10.8	...	...	14.1
XI.	38.4	38	......	0.5	1.2	1.6	2.1	2.6	3.1	3.8	4.3	5.0	5.6	6.4	7.1	8.1	9.4	11.2	14.3	...	...	12.9
XII.	43.0	39	......	...	...	...	...	...	1.8	1.95	2.1	2.3	2.6	2.8	3.2	3.7	4.0	4.7	5.2	...	...	31.0
XIII.	38.4	38	19 $ZnCl_2$	...	...	...	0.8	0.9	1.0	1.2	1.4	1.5	1.7	2.0	2.2	2.4	2.6	2.9	3.4	...	...	47.8

When Heated to 80.1° with Chlorhydric Acid (38.4 per cent.) and 50 per cent. $ZnCl_2$.

	Percentage of chlorhydric acid.	Weight of liquid. Grams.	Added. Grams.	5 per cent.	10 per cent.	15 per cent.	20 per cent.	25 per cent.	30 per cent.	35 per cent.	40 per cent.	45 per cent.	50 per cent.	55 per cent.	60 per cent.	65 per cent.	70 per cent.	75 per cent.	Velocity constant.
XIV.	38.4	36	18 $ZnCl_2$	4.0	6.0	7.6	9.4	11.0	12.8	14.6	16.4	18.3	20.5	22.6	25.0	27.4	30.6	33.6	3.2

When Heated to 100° with Sulphuric Acid (50 per cent.).

	Percentage of chlorhydric acid.	Weight of liquid. Grams.	Added. Grams.	5 per cent.	10 per cent.	15 per cent.	20 per cent.	25 per cent.	30 per cent.	35 per cent.	40 per cent.	45 per cent.	50 per cent.	55 per cent.	60 per cent.	65 per cent.	70 per cent.	75 per cent.	80 per cent.	85 per cent.	Velocity constant.
XVI.	50.0	35	......	4.0	6.0	8.25	11.0	14.0	17.0	20.5	24.0	29.0	33.5	38.5	44.0	50.0	57.5	65.5	76.5	94.0	2.1

tions of an hour required to decompose 5, 10, 15, etc., per cent. of the sulphonic acid.

The last column gives the velocity constants calculated, not from the figures of the table, but from the means of the constants given by each experimental measure, rejecting those of less than 10 and more than 80 per cent. decomposition, because at the two extremities the results are less accurate.

A very remarkable relation appears between the velocity constants and the concentration of the chlorhydric acid which promotes the action (as a catalysor?).

For the percentages of HCl between 13 and 31 the velocity increases fourfold for each successive increment of 6 per cent. HCl. The rate appears to be less rapid for higher percentages, but the upper limit of the law may perhaps be extended by more careful measures. Unpublished experiments confirm this relation for other sulphonic acids and extend it to lower percentages of HCl.

Mathematically stated, the relation is expressed by the formula: the logarithm of the velocity constant is a linear function of the percentage concentration of chlorhydric acid.

Since the sulphonic acids have nearly as strong a chemical affinity as chlorhydric acid, it was thought that they might catalyze themselves, and the decomposition might be related to the concentration. Only two experiments have been made, but they serve to confirm this idea :

1. Five grams metaxylenesulphonic acid were dissolved in 2.5 grams of water, and were heated at 100° for forty hours. The sulphuric acid set free was 1.9 per cent. of the amount corresponding to complete decomposition. No xylene was visible in the tube, but it separated out on diluting with water.

2. Five grams of metaxylenesulphonic acid were dissolved in 100 grams water and heated to 100° for forty hours. The sulphuric acid set free was only 0.1 per cent. Thus concentration in these experiments gives rise to a rapidly increasing rate of decomposition.

With metaxylenesulphonic acid a change of position of the SO_3H group, if such change can be brought about catalytically, would complicate the reaction, since the susceptibility to decomposition is greatly increased, when the SO_3H group is placed between the two side-chains.

The series of experiments will be extended to other tempera-

tures and the more tedious, but likewise more accurate, method of weighing the sulphuric acid set free instead of measuring the amount of hydrocarbon will be used.

If we attempt to estimate the differences and the similarities in the modes of catalytic action of strong acids in concentrated or in weak solutions, it will be convenient to do so under the headings of Ostwald's definition of catalysis.

1. *Reactions Which Are Accelerated or Retarded by Catalysis Take Place Also without a Catalysor.*—Experiments are evidently impossible with substances which take years for the transformation of 1 per cent., and conclusions can usually only be drawn from the form of reaction curves of measurable velocities, but it appears probable that the regularity of the decomposition of sulphonic acids without by-products will make it possible to obtain useful observations near the border line, where the action is almost imperceptible.

2. *Reactions in Opposite Directions Leading to an Equilibrium Must Be Equally Influenced by Catalysis.*—The hydrolysis of sulphonic acids in presence of sulphuric acid and water would belong under this rule if the reaction were reversible, but this is probably not the case since the synthesis is direct, while the decomposition is indirect by influence of H_2SO_4 (catalysis?). The data for 50 per cent. sulphuric acid given in the preceding table show that the limit of the action is very near complete decomposition, 88 per cent., while experiments made by heating xylene with sulphuric acid of 50 per cent. concentration to 100° proved that the reverse action does not take place perceptibly.

Even the action of a 75 per cent. sulphuric acid solution on xylene is an exceedingly slow one and stops when only a few per cent. of the xylene are transformed into the sulphonic acid. The hydrolysis of sulphonic acids by means of chlorhydric acid tends to complete decomposition, nor can any evidence be obtained of an inverse reaction.

3. *The Catalytic Influence is Nearly Proportional to the Concentration of the Catalysor.*—The chief object of this paper is to show that this rule does not apply to the case of concentrated acids, and that here the facts are directly opposed to the assumption that hydrolysis is caused by hydrogen ions. In the experiments cited the relation between concentration of acid and effect rises like the tension of a gas partially combined with water and the

effect of high concentration in aqueous solution of chlorhydric acid alone, and especially with addition of zinc chloride, recalls the activity imparted to gases condensed on platinum or palladium.   Ostwald discusses the action of these metals under the same heading as catalysis attributed to the ions of hydrogen, iron, manganese, etc., and OH ions, and also places ferments and enzymes beside them, saying there is no great doubt that the laws governing the action of these bodies are not essentially different from those of inorganic catalysors.

Taking these definitions together, they apply in very few points to the case of hydrolysis by concentrated acids.

The question of ionic dissociation presents new aspects in this case.   Usually the compounds subjected to catalysis have been like sugar and esters, incapable of any marked degree of dissociation in aqueous solution.   The sulphonic acids, on the contrary, are dissociated to nearly the same degree as the strongest acids, when in dilute solution, and although very little is known of the dissociation of strong acids in concentrated solution, it well may be considerable.   If hydrolysis only takes place upon undissociated molecules, then the increased rapidity due to high concentration of the acid solution and to addition of zinc chloride may be ascribed to the prevention of the dissociation of the catalyzed body, while that of the catalysor subsists to a certain degree.

Experiments at different temperatures and with more sensitive bodies like mesitylenesulphonic acid which acts at low temperatures and with weaker acids, may throw some light upon this subject.

The usefulness is evident of a minute study of the difference of behavior of the sulphonic acids, for it may obviously lead to methods of separation of the hydrocarbons and the acids.   Several authors have described such methods for the separation of meta- and paraxylene, and I have found during this series of experiments that mesitylenesulphonic acid, when heated to 80° for fifteen minutes with 38 per cent. chlorhydric acid, is almost wholly decomposed, while pseudocumenesulphonic acid, heated under the same circumstances, gives no sign of the separation of pseudocumene after five hours.   Armstrong has used this difference of action to separate the two hydrocarbons by heating their sulphonic acids with chlorhydric acid at 100°, but the statement attributed to him in Beilstein II, 29, is incorrect ; namely, that

pseudocumenesulphonic acid is not decomposed by heating for one hour with strong chlorhydric acid at 100°. There is difficulty in getting the rate for the first hour, because the pseudocumenesulphonic acid does not dissolve rapidly in strong chlorhydric acid at 100°, but the following determinations show the rate for subsequent hours :

Ten grams pseudocumenesulphonic acid, heated to 100°, with 35 grams chlorhydric acid (38.4 per cent. HCl), gave the following results :

Hours.	Pseudocumene. Per cent.	Hours.	Pseudocumene. Per cent.
1½	24.7	6½	95.9
2½	42.3	7½	101.6
3½	61.8	8½	103.8
4½	76.6	9½	100.3
5½	90.5	10½	100.3

The impossible results, 103.8 per cent., etc., may be due to the fact that a small amount of anhydrous sulphonic acid separates out and dissolves in the layer of hydrocarbon and is only slowly decomposed. All the results are too high for the same reason and a similar error, but a very small one, attaches to the preceding experiments with xylene. The fact that pseudocumenesulphonic acid loses a little water on long standing may also account for the above result.

Armstrong's observations were undoubtedly exact, but he is misquoted by Beilstein. He really states[1] that an oily layer is formed by adding water to the immediate product of the action of sulphuric acid upon pseudocumene and this oil, added to an equal volume of common chlorhydric acid, is not decomposed by heating one hour to 100°. No strength of acid is given, but the oily layer so described contains anhydrous pseudocumenesulphonic acid in solution in aqueous sulphuric acid, and the water present probably suffices to dilute the acids to the point where no perceptible decomposition takes place during one hour at 100°.

The name catalysis has been used after much hesitation, and it is only meant to imply that the rapidity of the action does not seem to be determined by the ordinary chemical forces of the bodies undergoing change, but rather that these forces are set in action in a peculiar way by an outside agent.

MASSACHUSETTS INSTITUTE OF
TECHNOLOGY, BOSTON,
February 26, 1901.

[1] Ber. d. chem. Ges., 11, 1697.

COMPOUNDS OF METHYL SULPHIDE WITH HALIDES OF METALS.

BY FRANCIS C. PHILLIPS.

WHEN methyl sulphide is added to a solution of palladium dichloride a voluminous yellow precipitate is produced, which is apparently flocculent, but upon microscopic examination is seen to consist of very fine indistinct crystals.

If the liquid containing the precipitate is heated, the precipitate redissolves, giving a liquid of a bright orange color. On cooling, this solution deposits orange-colored needle-shaped crystals which may be washed and dried, apparently without change, and are stable in air and unaffected by light. The crystals are quite soluble in boiling water, but very slightly soluble in the cold.

An analysis of the crystals was made in the following manner:

A portion of the substance was dissolved in water and a current of carbon monoxide passed through the solution, which was kept upon a water-bath. Metallic palladium was precipitated. This was filtered through an asbestos filter, previously weighed. After drying, the metal was heated in a stream of hydrogen, and then, without admitting air, dry nitrogen was passed through the tube, and the metal finally allowed to cool in the stream of nitrogen. Experiments demonstrated that the finely divided palladium could be thus easily brought to constant weight. The nitrogen used was prepared from air by the use of alkaline pyrogallate to remove oxygen, and subsequent passage over a heated mixture of copper and copper oxide. The hydrogen chloride in the filtrate from the palladium was neutralized by zinc and the chlorine then determined volumetrically by silver nitrate solution.

The determination of sulphur presented difficulties. Many experiments were made in attempts to oxidize the sulphur of the compound to sulphuric acid by fusion with various mixtures of alkaline carbonate with nitrate and chlorate, and with sodium peroxide. All these experiments proved fruitless, as in every case a portion of the sulphur was lost by volatilization. Heating with nitric acid in a sealed tube, failed to yield complete oxidation, even at temperatures which involved danger to the tube. The ordinary reagents which might be looked to for the

conversion of sulphur into sulphuric acid, are of little use in the case of alkyl sulphides and their compounds. The most feasible method seemed to be by direct combustion in oxygen, and this was attempted in the following manner : The substance contained in a porcelain boat was placed in a porcelain combustion tube which was heated to a high temperature in a furnace. The front end of this tube passed through a cork in the neck of a nitrogen flask, containing a solution of sodium hypobromite. To permit of this mode of connection, it was necessary to place the furnace in a strongly inclined position. The products of the combustion passed through a roll of platinum gauze, 10 cm. long, rolled tightly, and completely filling the cross-section of the combustion tube. After passing the sodium hypobromite solution in the nitrogen flask, the products were led into a bottle of 7 liters' capacity containing a little bromine water. A soft cork, soaked in melted spermaceti, served to connect the side tube of the nitrogen flask with that leading into the large bottle. Thus rubber tube connections were wholly avoided. The sodium hypobromite solution together with the washings of the large bottle and combustion tube were acidulated, evaporated, and the sulphur determined by weighing as barium sulphate.

Experiments were tried also in heating the methyl sulphide compound in carefully purified hydrogen. The same apparatus and reagents were used as in case of the employment of oxygen, the hydrogen sulphide produced being then oxidized by the sodium hypobromite to sulphuric acid. There seems, however, to be some danger of dissociation of the hydrogen sulphide and possible deposition of sulphur in the colder parts of the combustion tube. Determinations by the methods described yielded the following results :

	Per cent.
Palladium	35.09
	35.19
Chlorine	23.75
	23.57
	23.65
Sulphur	21.57
	21.40
	21.41

The analytical results indicate for the compound the composition $PdCl_2 2(CH_3)_2S$, the calculated percentages in the case of such a compound being :

	Per cent.
Palladium	35.41
Chlorine	23.46
Sulphur	21.22

The above formula is similar to that given by Enebuske[1] to the compound of methyl sulphide with platinous chloride, $PtCl_22(CH_3)_2S$. The palladium chloride methyl sulphide is quite stable in solid form. In solution it is susceptible to the same changes as those undergone by palladium dichloride. In solution it is reduced by carbon monoxide and more slowly also by hydrogen. In the solid state it is reduced by hydrogen in the cold, with setting free of methyl sulphide and hydrogen chloride.

One hundred grams of water dissolved at 26.1° C., 0.15 gram of the compound. The solution in water and also the dry substance possess a slight odor of methyl sulphide. It is soluble in a great number of organic liquids, including benzene, ether, alcohol, chloroform, acetone, ethylene dibromide, carbon disulphide, methyl iodide, commercial amylene, and gasoline. It fuses at 124° C., solidifying again on cooling to a red crystalline mass. It seemed to be of interest to learn something of the products of its decomposition by heat. For this purpose, it was heated in nitrogen. At 210° an evolution of methyl sulphide began, and continued until the temperature rose to 260°, when a black residue was left, which proved on analysis to consist of nearly pure palladious sulphide. The gas escaping at the higher temperature, after being passed through water to remove any hydrogen chloride which might be present, was led through a glass tube containing sodium carbonate heated to redness. The sodium carbonate was afterwards tested and found to have absorbed chlorine. When the escaping gas was led through a solution of potassium hydrosulphide, methyl hydrosulphide was easily detected by its reactions toward ammoniacal solutions of silver nitrate and of copper sulphate. It was found that hydrogen chloride is not evolved on heating the compound. Hence, as chlorine had been found, and also the radical methyl, the compound methyl chloride was indicated. Moderately heated, therefore, the compound yields up a portion of its methyl sulphide. At a more intense heat it yields methyl chloride, palladium sulphide remaining as a residue.

As regards the constitution of the compound, it would seem

[1] J. prakt. Chem., [2], 38, 358 (1888).

that the sulphur of the methyl sulphide might be tetravalent. The formula might possibly be written:

$$\underset{\displaystyle (CH_3)_2=S}{\overset{\displaystyle Cl}{\overset{\displaystyle |}{}}}\,\,—Pd—\,\,\underset{\displaystyle S=(CH_3)_2.}{\overset{\displaystyle Cl}{\overset{\displaystyle |}{}}}$$
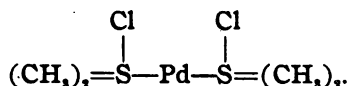
This is improbable, however, because the compound seems to contain chlorine linked with palladium, since hydrogen reduces the dry compound in the cold, just as it reduces dry palladium chloride, yielding hydrogen chloride in both cases.

It seemed to be of interest to study other compounds of methyl sulphide with halides of metals. The literature of the subject is scanty, little attention having been given to compounds of this class, since Loir[1] in 1853 described the compounds of methyl sulphide with mercuric chloride and iodide, and with platinic chloride.

For the preparation of the compounds described in this paper, it was necessary to obtain pure methyl sulphide. This was made by the method of Klason,[2] by distilling a mixture of sodium methyl sulphate with sodium sulphide.

COMPOUND OF METHYL SULPHIDE WITH MERCURIC CHLORIDE.

On adding methyl sulphide to a solution of mercuric chloride, a bulky precipitate of a white color is produced, which is seen under the microscope to be made up of indistinct crystalline needles. Exposed in a dry state to sunlight, the substance becomes somewhat darker in color. If preserved for some time in the solution in which it has been formed, it assumes a much more decidedly crystalline character. It is slightly soluble in water and more soluble in alcohol. The solution has a slight odor of methyl sulphide. It is slightly soluble in chloroform, carbon disulphide, ethylene dibromide, commercial amylene, benzene, acetone, and in petroleum gasoline. The solution in water yields a heavy yellow precipitate with caustic alkalies, and in other respects, the reactions in solution are similar to those of mercuric chloride.

Its melting-point varies with the rate of heating, as it undergoes partial decomposition, losing some of its methyl sulphide. When heated rather rapidly the lowest melting-point observed was 150°–151°, but if the heat is applied more slowly, its color

[1] *Ann. Chem. u. Pharm.*, **87**, 369 (1853) ; *Compt. rend.*, **34**, 1095.
[2] *Ber. d. chem. Ges.*, (1887), 3406.

grows darker, and as the result of a partial decomposition it melts at a varying and much higher temperature.

Heated in purified nitrogen it gives off methyl sulphide at about 150°, and at 170° white needle-shaped crystals form as a sublimate. No sulphide of mercury is formed as a result of heating. In the analysis of the compound the sulphur was determined by combustion in oxygen, as described in case of the palladium compound. Mercury was determined by precipitation of the aqueous solution by hydrogen sulphide and weighing as mercuric sulphide. Chlorine was determined by decomposition of the compound by zinc in presence of water and titration by silver nitrate solution. The results of the analysis are as follows:

	Per cent.
Mercury .	64.27
	64.07
	64.19
Chlorine	22.26
	22.68
	22.66
Sulphur	6.63
	6.84
	6.76
	6.73

Other determinations were made in the case of the same compound after crystallizing from alcohol. The results were:

	Per cent.
Mercury	64.41
	64.31
Chlorine	22.60
	22.53

The calculated percentages in the case of a compound having the formula $3HgCl_2,2(CH_3)_2S$ are as follows:

Mercury	64.63
Chlorine	22.70
Sulphur	6.42

Loir[1] assigns to the compound, obtained on adding methyl sulphide to mercuric chloride, the formula $HgCl_2(CH_3)_2S$. Analyses have been made of many preparations of the mercuric chloride methyl sulphide compound, but in no case has a product been obtained having the composition stated by Loir.

[1] *Loc. cit.*

COMPOUND OF METHYL SULPHIDE WITH CUPROUS CHLORIDE.

When methyl sulphide is added to a concentrated solution of cupric chloride, the color of the liquid changes from green to dark brown, and heat is evolved.   After standing for a few hours, a mass of white crystalline scales forms at the bottom.   The compound, if rapidly washed and dried, is white, but it is liable to turn to a yellowish green during drying.   Exclusion of air does not serve completely to prevent this change of color.   The crystals are almost insoluble in water, and are very slightly soluble in the various organic liquids mentioned in connection with the mercury compound.   Boiling with water seems to expel part of the methyl sulphide.   The substance dissolves in ammonia and in nitric acid.

Caustic alkalies decompose it, yielding an insoluble brownish red powder.   Digestion of the substance with hydrogen sulphide, gradually changes it to copper sulphide.   This reaction was made use of for a determination of the copper, the sulphide being ignited, redissolved, precipitated by sodium hydroxide, and weighed as cupric oxide.   Chlorine was determined in the filtrate from the copper sulphide by the method already mentioned.   As there seemed to be a possibility that the chlorine might be linked to carbon rather than to copper, and that consequently it might not be fully set free as hydrochloric acid in decomposing the compound by hydrogen sulphide, determinations were also made by heating the substance in a combustion tube traversed by a stream of hydrogen, absorption of the hydrogen chloride produced in water, neutralization by zinc and titration by silver nitrate solution.   Determinations were also made by decomposition of the copper chloride compound by magnesium powder and titration of the chlorine as magnesium chloride.   Sulphur was determined by the method of combustion in oxygen already described.   The results of analysis were as follows :

	Per cent.	
Copper	39.12	
	39.13	
Chlorine	21.85	Decomposition of the compound
	21.80	by hydrogen sulphide.
	21.76	Decomposition by magnesium.
	21.77	
	21.76	Decomposition by heating in
	21.60	hydrogen.
Sulphur	19.62	
	19.70	

The calculated percentages of the constituents named in the case of a compound having the composition $CuCl(CH_3)_2S$ are :

	Per cent.
Copper	39.46
Chlorine	22.00
Sulphur	19.90

Cuprous chloride methyl sulphide heated in nitrogen gives off methyl sulphide at about 100° C., and continues to lose methyl sulphide until the temperature reaches about 200° C. After heating to a somewhat higher temperature the chlorine present in the residue in one experiment was found to amount to 21.53 per cent. of the original weight of the portion of the compound employed.

At a temperature above 400° the compound yields a mixture of copper sulphide and copper in wire form. The reaction occurring between methyl sulphide and the solution of cupric chloride which leads to the formation of the compound $CuCl(CH_3)_2S$, is characterized by great intensity as evidenced by the heat evolved and by the promptness of the change. One-half of the chlorine in the cupric chloride is eliminated and in its stead methyl sulphide becomes linked to the copper. Apparently, therefore, the substance resulting should be a cupric compound. Judged by its white color and its chemical properties it is, apparently, to be classed as a cuprous and not as a cupric compound. Yet it does not seem probable that the copper atoms can be in this case linked as is supposed to

be the case in cuprous chloride,
$$\begin{array}{c} Cu-Cl \\ | \\ Cu-Cl \end{array}$$
The constitution of the compound might perhaps be expressed by the formula

$$\begin{array}{c} Cu-Cl \\ | \\ S=(CH_3)_2 \\ | \\ S=(CH_3)_2 \\ | \\ Cu-Cl \end{array}$$
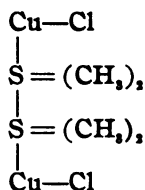
in which the sulphur appears to be tetravalent. The copper atom is no doubt linked more firmly to the chlorine than to the sulphur of the methyl sulphide. The question as to the classification of the compound as cuprous or cupric, seems to depend merely on whether there are one or two carbon atoms linked to

the copper atom. The linking of a chlorine atom, together with the sulphur atom of a methyl sulphide group to a copper atom, seems to impart to the compound a cuprous character as if the chlorine atom alone were present.

COMPOUND OF METHYL SULPHIDE WITH GOLD CHLORIDE.

When methyl sulphide is added to a solution of auric chloride, much heat is evolved, and an escape of hydrogen chloride occurs while an apparently flocculent white precipitate is produced. This precipitate is insoluble in water, but slightly soluble in alcohol. It may be washed and dried at room temperature by gas light. It is rapidly decomposed by sunlight, yielding metallic gold, methyl sulphide, and hydrogen chloride. If preserved in a dark place for a few weeks in the solution in which it was formed, and in presence of a slight excess of methyl sulphide, it assumes the shape of colorless crystalline needles.

It dissolves in various organic liquids, but the solutions soon deposit metallic gold. A determination of gold was made by exposing the substance under water to direct sunlight. The gold was rapidly reduced and was filtered out, burnt, and weighed in the metallic state. The chlorine was determined volumetrically in the filtrate from the gold. The sulphur was determined by combustion in oxygen, and weighing as barium sulphate.

The following analytical results were obtained :

	Per cent.
Gold	67.16
	66.98
	66.77
	67.42
Chlorine	12.32
	12.35
	11.97
	11.74
Sulphur	10.99
	10.88

These results suggest the composition $Au\begin{smallmatrix}Cl\\S(CH_3)_2\end{smallmatrix}$, since calculation shows that such a compound would contain :

	Per cent.
Gold	66.90
Chlorine	12.02
Sulphur	10.87

The gold compound was heated in nitrogen, when it was found that an evolution of methyl sulphide begins at about 100° and continues until the temperature approaches 200°. At higher temperature, pure gold is left as a residue.

The reaction leading to the formation of the gold compound resembles that by which the copper compound is produced, in that the auric chloride undergoes reduction, and the aurous chloride then unites with methyl sulphide. A trivalent gold atom appears to have its affinities satisfied partly by a chlorine atom, and partly by the sulphur atom of a methyl sulphide group.

It seems that in the compounds which have been here mentioned the metal is more firmly linked to the halogen than to the sulphur of the methyl sulphide, and that the part played by the methyl sulphide is somewhat like that of water in various hydrated salts. Ferrous chloride remains a ferrous compound no matter what may be the number of water molecules with which it combines.

Hydrated magnesium chloride is well known to lose hydrochloric acid on strong heating and in a somewhat analogous fashion some of the compounds of metallic halides with methyl sulphide decompose on heating into metallic sulphide and methyl chloride.

A further study of compounds of alkyl sulphide with other metallic halides is in hand.

My acknowledgments are due to Mr. J. C. Fetterman, assistant in this laboratory, for his skill and careful attention to details in conducting many difficult and somewhat tedious analyses in connection with this work.

A NEW METHOD FOR THE ESTIMATION OF SOLUBLE NITROCELLULOSE IN GUNCOTTON AND SMOKELESS POWDER.

BY K. B. QUINAN.

A SHORT review of the methods now in use for the estimation of soluble nitrocellulose in guncotton and smokeless powder may be of interest to those who are not familiar with the subject under consideration. For this reason a brief description will be given here of the two methods most generally in use ; namely, the (so-called) aliquot method, and the residual method which is

at present in use by the United States government as the official method.

The first-named method is essentially as follows : A weighed portion, about 1 gram, of the dried and finely divided sample of guncotton, or colloided powder is placed in a vessel of suitable shape, provided with a tight glass stopper, and is treated therein with 250 cc. of a mixture of ether-alcohol 2 : 1 by volume. The contents of the vessel are thoroughly agitated by shaking until all the soluble nitrocellulose is in solution. An aliquot portion of this solution is now taken and placed in a small tared Erlenmeyer flask, of about 100 cc. capacity, and is evaporated to dryness therein at a temperature of 65.5° C., the final drying being made at 100° C. The Erlenmeyer flask is now cooled and weighed and the percentage of soluble nitrocellulose calculated from the weight of the colloid so obtained.

Although this method, as used in this laboratory, gives very accurate results, the opportunities for errors are many and various, and it requires much care to avoid them.

The second method, referred to as the residual method, gives very unsatisfactory results. It is essentially as follows (taken verbatim from the United States government syllabus) : "About 1.5 grams of the finely divided, dry sample are treated in a covered beaker or other suitable vessel, with 250 cc. of a mixture of 1 volume absolute alcohol, C. P., and 2 volumes of strongest ether, C. P., with frequent stirring, for not less than two hours. (Four hours are frequently necessary for complete solution.) The vessel is kept covered to prevent loss by evaporation. The residue is allowed to settle and the supernatant liquid decanted through an asbestos filter, made from well purified asbestos fiber. The filter is placed in the neck of a flask or otherwise protected to avoid loss of solvent by evaporation during filtration.

"The residue in the flask is then treated with a further quantity of 200 cc. of ether-alcohol mixture, and again thoroughly stirred until extraction is complete ; and the whole mass is then settled. The clear liquid may be decanted, and the remainder filtered through the asbestos fiber and well washed by successive portions of ether-alcohol. The filter is then partially dried at 40° C., and the drying completed by exposure to a temperature of 100° C. for two hours. The loss (minus any volatile matter, if present) represents soluble nitrocellulose."

The main difficulty encountered in the operation of this method is the filtration of the thick colloid formed by the guncotton and ether-alcohol. It is practically impossible to effect the passage of the thick colloid through an asbestos filter without the aid of great pressure, and a large expenditure of valuable time, for the filtration is extremely slow even under the most favorable conditions. Another strong objection to the method lies in the fact that it usually requires four or five days for the completion of an analysis by this method, which renders it practically valueless for manufacturers.

The above outlined syllabi are merely intended to convey a general idea of the methods in use, and to show in a general way the objections to each method. It was to overcome these objectionable features in the methods above described that the following method was devised by the writer, which may be termed the "centrifugal method."

As far as the author is aware, the theory of centrifugal sedimentation has never as yet been applied to this particular subject. The application of this theory to the analysis of smokeless powder is as follows :

APPARATUS.

The apparatus consists of a centrifugal machine, essentially as

Fig. 3

Fig. 1

Fig. 2

Fig. 4
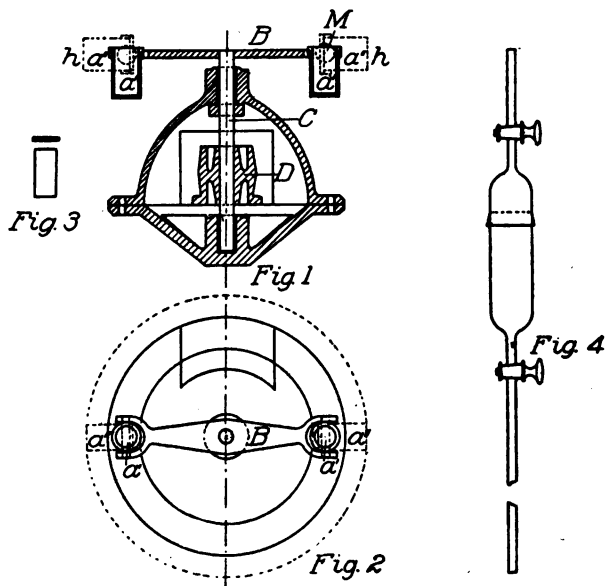
per attached sketch.   The vertical driving shaft (C) carries at its upper extremity a horizontal arm (B), at its lower extremity the driving pulley (D).   To each end of the horizontal arm (B) are attached adjustable cups ($a'a'$) arranged on side pivots, so that they may assume a horizontal position when in motion.

	Length.	Diam.	Width.	Depth.	Thick.	Material.
Driving shaft (C)..	16½″	1¼″	......	,......	..	Machine steel
Horizontal arm (B)	17″	......	{ max 3½″ { min 1¼″	......	¼″	Forged steel
Pulley (D).......	..	4¼″	5″	......	..	Cast iron
Fixed cups ($a'a'$).	..	inside–2″	......	inside–4″	..	Steel
Bearing (M)......	..	¼″	¼″	......	..	Steel

Revolutions per minute of arm (B).................... 2000
Total centrifugal force at (h) .... 450 lb. (about)
Power required .... ¼ H. P. (about)
Cost of construction .... $110.00 (approx.)

	Diam. Int.	Depth. Int.	Thickness of walls.		Weight.
Aluminum cups, Fig. 3.	1.9″	4¼″	1/100″	Plane bottom	1½ oz. max.

	Length over all.	Length of bulb.	Diameter of bulb.	Length between cocks.	Material.
Vacuum pipette, Fig. 4.	25½″	6½″	1¼″	10″	Glass

OPERATION.

About 1 gram of the finely divided (dry) sample of guncotton or smokeless powder, which is to be analyzed, is weighed on a watch-glass and is transferred to the aluminum vessel (Fig. 3) which has previously been thoroughly cleansed and dried.   (Or the sample may be weighed into the aluminum vessel direct, if so desired.)   To this is added 50 cc. of alcohol and the sample is thoroughly stirred to bring it into suspension.   100 cc. of ether are now added to the mixture in the cup, and the whole is, then stirred for several minutes.[1]   After removing the stirring rod, the aluminum vessel containing the solution is placed in· one of the cups ($a'a'$) of the centrifugal machine (Fig. 1) and is covered by a loosely fitting aluminum cap.   In the other cup of the centrifugal machine is placed a second aluminum vessel, containing a second sample which has been treated in the above described manner.   (In this way two determinations may be carried on at the same time.)   The centrifugal machine is now started gradually and allowed to remain running at top speed for ten to twelve minutes.   This has been found to be a sufficient length of time for the complete sedimentation of all in-

[1] See last paragraph as to solvents.

soluble matter in the solution. The machine is now stopped gradually, and the aluminum vessels are removed from the cups (a'a') and placed in a convenient position before the operator. All insoluble matter will now be found in the bottom of the aluminum vessels, and the perfectly clear supernatant liquid may be drawn off to within a quarter of an inch of the bottom of the aluminum vessels. This is done by means of the vacuum pipette shown in Fig. 4. The air in the bulb of this pipette is exhausted by means of an air-pump before use. The advantage gained by using the vacuum pipette is very easily seen, for when the lower end of the pipette is submerged in the clear liquid in the aluminum vessel and the lower stop-cock is opened, the clear solution from the vessel at once rises in the tube and passes into the bulb of the pipette. By lowering the pipette from time to time, nearly all the supernatant liquid may be drawn up into the bulb without disturbing the precipitate in the bottom of the vessel. If, however, the precipitate is disturbed it will at once be noticed as it rises in the tube clouding the clear liquid. If this should take place, the lower valve is immediately closed, thus preventing the access of the insoluble matter to the clear liquid in the bulb. The upper valve is now opened, thus releasing the tension in the bulb, so that when the lower valve is cautiously opened and a few drops of the liquid are allowed to run out of the tube and into the aluminum vessel, they carry with them all suspended matter which may have been drawn into the tube. In this way all opportunity for loss of insoluble matter is avoided. There now remains in the aluminum vessels about 10 or 15 cc. of colloid solution and a film of insoluble matter on the bottom of the vessels. Stir this insoluble matter up from the bottom of the vessel with a glass stirring rod, wash the rod thoroughly by means of a wash-bottle filled with pure ether-alcohol, and at the same time rinse down the sides of the aluminum vessels with the ether-alcohol from the wash-bottle. Now add about 50 to 75 cc. of fresh ether-alcohol to the mixture in the vessels, stir it up, place in the centrifugal, and again proceed in the manner already described. This operation should be repeated several times until all traces of soluble matter have been removed. Seven or eight washings usually suffice to remove entirely all soluble matter. Samples containing a high percentage of insoluble matter may require twelve or more washings to complete extraction.

After the extraction has been completed the insoluble matter is transferred to a weighed Gooch crucible provided with the usual asbestos pad, is dried therein at 100° C., and weighed. If preferred, the insoluble matter may be dried and weighed directly in the aluminum vessel in which the extraction was performed. The only objection to drying and weighing directly in the aluminum vessel is that this vessel cannot be ignited.

The whole time required for an analysis by this method, exclusive of the time required for drying, is from one to two hours. The average time which has been found necessary to complete an analysis is about one and one-quarter hours, for it will readily be seen that in each successive extraction, the viscosity of the solution decreases, and consequently the sedimentation is much more rapid toward the end of the analysis than it was in the beginning. For instance, the first solution obtained is a thick colloid and requires about ten or twelve minutes in the centrifugal for sedimentation, but with the second solution, about eight minutes in the machine will suffice.

This method is equally applicable to the estimation of acetone-soluble nitrocellulose, the operation being the same as in the case of the ether-alcohol extraction already described.

The results obtained by this method have been highly satisfactory both for accuracy and rapidity.

The following analyses were made on a sample of nitrocellulose containing a known amount of insoluble matter :

No. of analysis.	Insoluble matter found. Per cent.	Insoluble matter required. Per cent.
2664	0.54	0.69
2665	0.50	(Determined by aliquot method.)
2666	0.59	
2667	0.53	

These results may be improved upon by further experience with the method.

In laboratories where power is not available, the form of the centrifugal machine herein described may be modified, and provided with gear so as to admit of its being run by hand. The use of power is, of course, preferable. This syllabus is based upon the results obtained with a machine of the dimensions herein described.

In order to make the laboratory analysis analogous to the process of manufacture, the solvents used should be of the same

strength as those ordinarily used in manufacture. Care must be taken, however, that the solvents are free from all matter not volatile at 100° C.

COMPOSITION OF TEXAS PETROLEUM.

BY CHARLES F. MABERY.

INDICATIONS of the presence of petroleum in Texas in several sections have been observed during the last thirty years, and many attempts have been made to obtain oil in sufficient quantities for the preparation of commercial products. But it is only within the last six years that oil has been found in sufficient amounts to encourage further development. The principal yield has been in the counties of Navarro, Bexar, Nacagdoches, and Hardin, and the chief supply has come from the Corsicana field in Navarro County. In the early development of the Corsicana field a specimen of the oil was briefly examined by Thiele,[1] who gave its specific gravity as 0.8296, and the proportions in temperatures Fahrenheit in which it distilled. The resemblance of this oil to Pennsylvania and to Ohio petroleum alluded to by the author seems to be scarcely supported by the meager examination.

Corsicana oil was later examined by Richardson,[2] who obtained percentages of carbon and hydrogen in the distillate 100°–150° at 2.5 mm., corresponding to the series C_nH_{2n}.

Another important section of the Texas oil field has recently been developed in Jefferson County, and it has suddenly become famous by the discovery of a large pool, under high pressure, that has furnished the phenomenal supply in the Lucas well. The surface indications in this section, in the vicinity of Sabine Pass, were such that this pool narrowly escaped previous discovery by other prospectors. Oil has been obtained in smaller amounts for some time in this county, and the composition of one specimen was ascertained by Mabery and Buck.[3] This oil was found to consist mainly of the series of hydrocarbons represented by the general symbols C_nH_{2n-2} and C_nH_{2n-4}. It was an extremely heavy petroleum, specific gravity 0.9500. Scarcely any distilled below

[1] Am. Chem. J., 22, 489.
[2] J. Soc. Chem. Ind.. February, 1900.
[3] This Journal, 22, 553.

250° atmospheric pressure. Having obtained a quantity of oil from the Lucas well before it was capped, I was interested to ascertain its composition. The well was drilled to a depth variously estimated between 1000 and 1300 feet at a point where the surface was approximately 1100 feet above sea-level, consequently the oil pool was probably 200 feet below sea-level. A peculiar method of drilling was necessary in penetrating the wet surface soil and 400 feet of drift sand. When the oil was reached, the four-inch casing weighing 6 tons was driven out with such force that it was sent 200 feet into the air and the column of oil which followed escaped in such quantities that the daily output before the well was capped was estimated at 70,000 barrels.

When received fresh from the well this oil gave a strong odor of hydrogen sulphide. Its specific gravity at 20° was 0.920, corresponding to 22° B., showing it to be heavier than the Corsicana oil, but not so heavy as other specimens of Texas oil examined in this laboratory. It is a high sulphur oil (2.16 per cent.), perhaps the highest in sulphur of any petroleum I have examined. It contains considerable nitrogen, more than 1 per cent. Under atmospheric pressure, it distilled in the following proportions:

	145°-200°.	200°-250°.
Per cent	4	11
Baumé	46°	35°

Under 14 mm. it distilled as follows:

	95°-100°.	150°-200°.	250°-300°.	Residue.
Per cent	17	17	51	15
Baumé	29°	25°	17°	14°

The vacuum distillation was continued until considerable proportions collected at certain temperatures. To determine the series, the distillates 130°–135°, 155°–160°, 190°–195°, were selected for examination. The crude fractions were thoroughly purified with concentrated and with fuming sulphuric acid, and washed with caustic soda. The fraction 130°–135° gave as its specific gravity at 20°, 0.8553, the fraction 155°–160°, 0.8746, and the fraction 190°–195°, 0.8915. To determine the series, combustions were made of each of these oils. The fraction 130°–135° gave 86.86 per cent. carbon, and 13.27 per cent. hydrogen, which corresponds to the symbol $C_{12}H_{22}$, 86.75 per cent. carbon and 13.25 per cent. hydrogen. The molecular weight of this oil at the freezing-point of benzene was found to be 170. The formula $C_{12}H_{22}$ requires 160. The fraction 155°–160° gave 86.26 per cent.

carbon and 13.48 per cent. hydrogen ; required for the formula $C_{14}H_{22}$, carbon 86.60 per cent., hydrogen 13.40 per cent. The molecular weight of this fraction at the freezing-point of benzene was found to be 194.1 ; calculated for $C_{14}H_{26}$, 194. This formula was further confirmed by a determination of the index of refraction which gave 1.473, corresponding to the molecular refraction 62.36; calculated for the formula $C_{14}H_{20}$, 62.33. A combustion of the fraction 190°–195° gave 87.26 per cent. carbon and 12.54 per cent. hydrogen. The formula $C_{16}H_{30}$ requires 87.03 per cent. carbon, 12.97 per cent. hydrogen. The determination of the molecular weight of this fraction at the freezing-point of benzene gave 222.8 ; calculated for $C_{16}H_{30}$, 222. This formula was also confirmed by the index of refraction which gave 1.484, corresponding to the molecular refraction 71.64 ; required for the formula $C_{16}H_{30}$, 71.54. The principal hydrocarbons in this petroleum, therefore, are members of the series C_nH_{2n-2}, the same series that Mabery and Buck found in the other petroleum mentioned above, in the lower portions. Since the hydrocarbons in the two oils were fractioned under different pressures, the corresponding differences in temperatures shows an agreement in percentage composition and in molecular weights.

The residue from the last distillation in vacuo gave as its specific gravity 14° Baumé. This oil is, therefore, less rich in the heavier hydrocarbons that make the most valuable lubricators, and asphalts than the heavier Texas oil previously examined.

Since the hydrocarbons in this oil show no evidence of unsaturation, their structure is explained by the assumption of a double methylene ring and its derivatives. Such a structure would correspond to a dihexahydro diphenyl,

$$H_2C \underset{\substack{C\ \ C \\ H_2\ \ H_2}}{\overset{\substack{H_2\ \ H_2 \\ C\ \ C}}{\diamondsuit}} CH-HC \underset{\substack{C\ \ C \\ H_2\ \ H_2}}{\overset{\substack{H_2\ \ H_2 \\ C\ \ C}}{\diamondsuit}} CH_2 = C_{12}H_{22}.$$
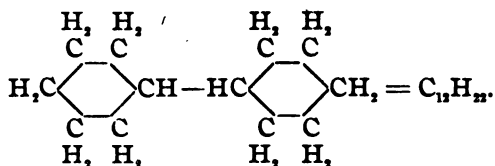
The hydrocarbon $C_{14}H_{26}$ should be a dimethyl or an ethyl derivative, and the hydrocarbon $C_{16}H_{30}$ could contain a single butyl side chain, or an equivalent in methyl, ethyl, or propyl side-chains. This homologous series of hydrocarbons presents an interesting field for study, since so little is known about them.

Mr. O. J. Sieplein, instructor, and Mr. A. H. Goldstein, student in this laboratory, have aided in the experimental work on this petroleum. Aid in carrying on this work was received from the C. M. Warren Fund for chemical research.

NOTES.

On Nitrometer Work.—The following work was done on the usual nitrometer, composed of a decomposing bulb and reservoir and the complement of a measuring tube, reduction tube and reservoir. The measuring tube had a capacity of 140 cc. The potassium nitrate used was Merck's, chemically pure, recrystallized. About 0.5 gram was used for each determination. The temperature of the laboratory, while the work was being done, was approximately 68° F. The dry potassium nitrate was weighed out into tared weighing bottles and about 15 cc. of sulphuric acid added. The bottles were then stoppered and set aside for about eighteen hours, or over night, by which time a clear solution was obtained, if the acid used was over 90 per cent. H_2SO_4, but if of less strength a residue, presumably of potassium sulphate, was left. The contents of the weighing-bottles were transferred to the decomposing bulb with the aid of a wash-bottle containing acid of the same strength as that used in the weighing bottles. In each determination 32 cc. of acid were used. The strengths of sulphuric acid used and the volume in cubic centimeters of nitric oxide (NO) per gram of potassium nitrate for each acid are as follows :

Strength of sulphuric acid in per cent.	Cubic centimeters of nitric oxide per gram potassium nitrate.					
	I.	II.	III.	IV.	V.	Average.
98.03	222.0	221.8	222.0	222.3	222.3	222.08
96.92	223.2	223.0	223.3	223.3	....	223.2
96.92	224.0	224.3	224.4	224.4	224.4	224.3
95.14	225.1	224.8	225.0	225.2	225.0	225.0
94.07	225.0	225.0	224.9	225.2	225.0	225.02
93.05	225.1	225.0	224.8	224.9	225.0	224.96
90.90	225.0	224.9	224.9	225.0	225.0	224.96
85.04	225.3	225.1	225.3	225.0	225.3	225.2
80.14	226.2	226.0	226.2	226.2	226.0	226.1

A difference of 4.02 cc. of nitric oxide is thus obtained by the use of the strongest and weakest acids. It seems probable that this is due to the varying absorptive powers for nitric oxide, of the different strengths of sulphuric acid used.

Lunge[1] states that "1 cc. of concentrated vitriol dissolves 0.000593 gram = 0.035 cc. NO." If this 4.02 cc. of nitric oxide per gram, or 2.01 per half gram of potassium nitrate is due to the difference of solubility of nitric oxide in the first and last acids used, then 32 cc. of 98.03 per cent. sulphuric acid absorbs 2.01 cc. nitric oxide and 1 cc. absorbs 0.0628 cc. nitric oxide. For nitrometer work acid of about 95 per cent. H_2SO_4 appears to be the best. Weaker acid attacks the mercury more readily and decomposes nitric acid more slowly. There is no objection to stronger acid except the difficulty of obtaining it. The chemically pure acid made by a well-known company has been found to vary from 95.0 to 98.0 per cent. H_2SO_4.

<div align="right">C. H. SHEPARD.</div>

CHEMICAL LABORATORY, UNION IRON WORKS,
SAN FRANCISCO, CAL.

NEW BOOKS.

A TEXT-BOOK OF IMPORTANT MINERALS AND ROCKS WITH TABLES FOR THE DETERMINATION OF MINERALS. BY S. E. TILLMAN. New York: John Wiley & Sons. 1900. viii + 196 pp. Price, $2.00.

The preface states that the author has designed this book especially for the course in mineralogy at the West Point Military Academy.

The subjects are presented in the order usual in most text-books. Crystallography is treated very briefly: The six systems are defined and illustrated by a few examples. Crystallographic symmetry is defined and contrasted with geometric symmetry. The chemical and physical properties of minerals are reviewed in a short chapter.

Chapter III devotes sixty-four pages to well written descriptions of about seventy-five species, including some well-known gems, ores of the metals, and the common rock-forming minerals.

With the descriptions brief but well selected notes are given as to the occurrence and economic value of many species.

The tables for the determination of minerals are based upon the more obvious physical characteristics and seem well adapted to aid a class in the study of a collection. The book closes with a classification of the common rocks.

The book would seem well adapted for a short practical course in mineralogy if in the hands of a good teacher, otherwise its

[1] *J. Soc. Chem. Ind.*, (1895), p. 447.

abundance of definitions would be out of proportion to its brevity
of explanation.   N. W. LORD.

ENGINEERING CHEMISTRY. A MANUAL OF QUANTITATIVE CHEMICAL
ANALYSIS, FOR THE USE OF STUDENTS, CHEMISTS, AND ENGINEERS.
BY THOMAS B. STILLMAN, M.Sc., PH.D., Professor of Analytical
Chemistry in the Stevens Institute of Technology. Second edition. With
132 illustrations. Easton, Pa.: The Chemical Publishing Company. 1900.
xxii + 503 pp. Price, $4.50.

The first edition of this work was published in 1897, and
reviewed in this Journal, in that year (p. 272). In this second
edition there has been a transposition of subject-matter so as to
bring under one heading, or chapter, the consideration of allied
subjects, formerly distributed throughout the volume. The addi-
tion of new matter is comparatively small. Some fifteen pages
of the first edition have been omitted. One of the valuable
characteristics of the work is the number of references to original
papers in American, English, German, and French scientific
journals. These references have been brought up to date in this
edition.

There are some few matters open to criticism. The author
only occasionally directs attention to the necessity of repeating
separations in gravimetric work, in order to obtain accurate
results. In some of his schemes of analysis phosphorus pentoxide
is weighed with, and calculated, as alumina. In the analysis of
gases by Hempel's apparatus the explosions are made over water,
a method Hempel himself has rejected. The table for Baumé's
hydrometer for liquids heavier than water, is entirely incorrect.

The work is particularly valuable in that it treats of both the
chemical and physical examination of many materials and factory
products that are rarely noticed in ordinary laboratory manuals.
In comparison with the downpour, we might almost say deluge,
of these latter, a manual of this kind is comparatively rare. All
that has been said in commendation of the work by the reviewer
of the first edition can certainly be endorsed. It is a valuable
book.   H. PEMBERTON, JR.

A MANUAL OF ASSAYING. BY ALFRED STANLEY MILLER. First edition.
New York: John Wiley & Sons. 1900. 91 pp. Price, $1.00.

This little book is to be recommended chiefly for its brevity
and clear style. The various methods of fire assaying are so
arranged and described as to afford in the minimum space a good,
general idea of the subject. It is weak, in common with many

similar works, in sometimes offering impracticable or not strictly correct directions on essential points and in describing methods not equal to those in actual use to-day. In other words, an operator with this book as a basis, would at the outset make but a slow and indifferent workman in an up-to-date assay office. This is, however, to a large extent, simply illustrative of the difference between school instruction and actual competitive practice, and the writer knows of no similar work that presents the subject in a general way more clearly and concisely.

The book is well printed in clear, large type and contains numerous illustrations.   ALBERT H. LOW.

A SCHOOL CHEMISTRY, INTENDED FOR USE IN HIGH SCHOOLS AND IN ELEMENTARY CLASSES IN COLLEGES. BY JOHN WADDELL. New York : The Macmillan Company. 1900. viii + 278 pp. Price, 90 cents.

The author assumes very properly, that most students fail to obtain clear notions of chemistry from their first course of lectures, or their early struggles with text-book and teacher, but he thinks that the users of this book will fare better than their predecessors. He hopes that the pupil will be able " to discover new facts, to see their connections, * * * to observe the important phenomena, and to understand their full significance." If his hopes should be realized, only partially, what a welcome would be accorded this recent addition to the crowded ranks of elementary text-books !

Five-sixths of the text is allotted to the non-metals, and of the metals only the most common are mentioned. Numerical data are less prominent than in most text-books, even of this class, and only with difficulty can a few problems be discovered. Perhaps the most noticeable features of the book are the clear statement of facts, and the efforts of the author to lead the pupil to observe closely and understandingly. His experience as a teacher and as an examiner, has enabled him to present the subject in a simple and interesting way, and a student who will read this book, make its experiments, and answer conscientiously its interrogations, should acquire a clear, and not insignificant, knowledge of the science and art of chemistry.   L. B. HALL.

ELEMENTARY ORGANIC ANALYSIS. FRANCIS GANO BENEDICT. Easton, Pa.: The Chemical Publishing Company. 1900. vi + 86 pp. Price, $1.00.

This manual gives clear and accurate directions for the determination of carbon and hydrogen in organic compounds by com-

¨bustion in a tube of glass, porcelain, or platinum. After a full discussion of the reagents and apparatus required for the analysis of compounds containing only these elements, the preparation of the tube and the process of combustion are described in an admirable manner. Directions then follow for the combustion of solids containing, besides carbon and hydrogen, nitrogen, the halogens, sulphur or the alkali metals, and also for the analysis of explosive, or difficultly combustible bodies, and liquids. The suggestions which accompany these directions are most valuable, while the numerous references to journals and text-books will be of the greatest assistance when new compounds are to be analyzed.

We believe this book will be helpful to all chemists who may have occasion to carry out the determinations mentioned above, and of still greater value to the student of little experience.

<div align="right">L. B. HALL.</div>

A HANDBOOK OF INDUSTRIAL ORGANIC CHEMISTRY. BY SAMUEL P. SADTLER, PH.D., F.C.S. Third edition. Philadelphia : J. B. Lippincott Co. 1900. 543 pp. Price, $5.00.

Chemists who have had an opportunity to use the earlier editions of Dr. Sadtler's excellent work will welcome most heartily this new edition. It represents more thoroughly than any similar publication the practice of the United States in the organic chemical industries and at the same time covers what is best in the European practice. Full justification is found for the statements of the preface to this edition to the effect that "every chapter has been revised and new matter added. * * * It has been sought to incorporate in this book all of this advance in our knowledge that is definitely acknowledged by chemists. The bibliography has in all chapters been brought down to date and the statistics are the most recent obtainable."

So we find, among other things, new mention and description of the forms of artificial silk, formaldehyde, tanning, dégras, Rohrmann's process for 90 to 100 per cent. acetic acid in one operation. S. B. Boulton's diagram, illustrating the process of distillation of coal, the latter curiously omitted, although mentioned, in the second edition is here introduced.

The matter presented is excellently and logically classified as in the former edition. Raw materials, processes of treatment, products, analytical tests and methods, bibliography and statistics follow each other in the order named. Raw materials and pro-

cesses of treatment are considered fully but in a general way and details often of the utmost importance to the manufacturer are omitted. Yet the information conveyed will be most useful to students and instructors, while the analytical tests and methods and the bibliography and statistics, since they have been brought to date, will be of great value and convenience to the general chemist and in many cases to specialists.

It is to be regretted that some of the later and more widely used forms of machinery have not been included in the illustrations of the book. For instance, in discussion of sugar manu-facture the vacuum evaporator of Yaryan is described at some length, while the more widely applicable forms of Wellner-Jelenek and of Swenson are not noticed. The Hepworth centrifugal is figured, but the Weston and the Lafferty forms are not mentioned. In the discussion of recovery coke ovens, the older Appolt and Simon-Carvés' ovens are described and the later Semet-Solvay and Otto-Hoffmann forms, the use of which is so widely extending, both in this country and in Germany, are mentioned only in the table of statistics. Yet it must not be forgotten that in such a volume, devoted to practically the entire field of organic industrial chemistry, space is limited and too much of it cannot be devoted to the various forms of machinery available for the several processes.

. Some embarrassing typographical errors, which have carried through the two editions, appear to have escaped the attention of the proof-readers, but they are not such as to be misleading. For instance, only the most inexperienced reader would be misled by the statement that starch '' is soluble in cold water, alcohol, ether,'' etc.

The book is made in the attractive style and finish of the Lippincott Company, is provided with an excellent table of contents, a list of illustrations, and an index, and is to be commended to the favorable consideration of instructors, students, and working chemists. WM. MCMURTRIE.

COMMERCIAL ORGANIC ANALYSIS. BY ALFRED H. ALLEN, F.I.C., F.C.S. VOL. III. PART I. TANNINS, DYES, AND COLORING-MATTERS, WRITING INKS. Third edition. Revised and edited by J. MERRITT MATTHEWS, Ph.D. Philadelphia: P. Blakiston's Son & Co. 1900. 589 pp. Price, $4.50.

Since the first edition of Mr. Allen's valuable work, its horizon has been considerably enlarged, and the value of the work largely

enhanced. Instead of being strictly a treatise on commercial organic analysis, it has taken on something of the character of a technology. It now treats not only of the tests and methods of estimation of organic substances of commercial value, and of methods for detecting adulterations in them, but it gives in many instances their history, chemical structure, and commercial methods of preparation.

Dr. Matthews has certainly proved himself a worthy successor to Mr. Allen's former collaborator, the late Dr. Leffmann, judging by his work in this volume which includes the tannins, dyes, coloring-matters, and writing inks, all of them subjects with which he is thoroughly familiar, practically as well as theoreti- cally.

The aromatic acids which were in Part I, Vol. III of the second edition, have been transferred to Part III, Vol. II of the third edition, which is in preparation.

The old material has been practically rewritten in bringing it up to date for this volume. The new tannin materials are described, and our best knowledge of tannin analysis, which is far from what it should be, is given in detail. The arrangement of the chapter on dyes and coloring-matters is entirely changed, making decided improvement, and the amount of material is largely increased. Eight pages, at the end of the volume, are devoted to the constitution and analysis of writing inks, and to the chemical examination of ink marks. Almost the whole of this matter is devoted to the iron inks with only a passing mention of the aniline writing fluids. · WM. L. DUDLEY.

CHEMICAL TECHNOLOGY OR CHEMISTRY IN ITS APPLICATION TO ARTS AND MANUFACTURES. EDITED BY CHAS. E. GROVES AND WM. THORP. VOL. III. GAS LIGHTING, BY CHAS. HUNT. Philadelphia: P. Blakiston's Son & Co. 1900. xviii+312 pp. Illus· Price, $3.50.

It is eleven years since the publication of the first volume of this work which treated of fuels ; and it was six years later that the second volume, on "Lighting by Solid and Liquid Illumi- nants," made its appearance.

The present volume discusses the manufacture, purification, and distribution of illuminating gas, and its application for light- ing purposes, much in the same manner as other works of its kind. The processes and methods refer mainly to English prac- tice.

It is not to be expected that an author can give within the compass of 300 pages, a complete statement of even the present condition of the gas industry and its collateral branches. The present volume, however, might have been considerably enlarged with great advantage, inasmuch as some subjects are treated inadequately or not at all.

Works of this character are, of necessity, largely made up of matter, which in some form has been published or discussed in the technical journals, and we should be much better equipped with such works of reference if there were fewer of them, but if those published treated the subjects in a more exhaustive manner.

The volume will be found of much value on many points connected with the gas industry. It is well printed and liberally illustrated. E. G. LOVE.

A TEXT-BOOK OF CHEMISTRY, INTENDED FOR THE USE OF PHARMACEUTICAL AND MEDICAL STUDENTS. BY SAMUEL P. SADTLER, Ph.D., F.C.S., and VIRGIL COBLENTZ, PH.D., F.C.S. In two vols. Philadelphia: J. B. Lippincott Co. 1900.

This is a revised and enlarged edition of the work brought out some years ago by Sadtler and Trimble. Volume I, which is devoted to physics, general and inorganic chemistry, and organic chemistry represents a third edition, while Volume II, on analytical chemistry, is a second edition.

In the presentation of the subject of chemistry to students of medicine and pharmacy it is extremely difficult to select the proper amount as well as the proper kind of information. In earlier attempts in this direction text-books offered to students in these specialties were characterized by a meagerness in detail and inaccuracy in statement which were discouraging to the teacher in search of a suitable manual for class instruction. Even yet we find books designated as "essentials" of chemistry for students of medicine and pharmacy.

But there is now great danger of going too far in the other direction in the production of text-books for these classes of students. The attempt is made to cover a little of everything in the field of chemistry and we have, as a result, treatises quite beyond the needs or capabilities of the embryo drug clerk or physician. If clearness and conciseness of statement are anywhere in order it certainly is in the chemical text-books for such students who are usually beginners, and who, as a rule, suffer

from the defects of irregular preliminary training. A text-book should not be allowed to grow into a large handbook, valuable for reference rather than for every-day study. It is not right that a school text-book to be placed in the hands of boys, beginning the study of chemistry in a college of medicine or pharmacy, should be filled up with the descriptive matters which properly belong in the pharmacopœia, the dispensatories or in a treatise on materia medica, to the exclusion of a clear discussion of the elementary principles of the science, without a knowledge of which, the medical student's notions of chemistry remain forever hazy and unsatisfactory.

The two large volumes before us contain much that is valuable but it appears to the writer that they err in the direction suggested by the last remarks. It is evident that they are written by practical men and on nearly every page of Volume I facts and figures are given which are well to know. Important data concerning hundreds, perhaps thousands, of compounds are included, making of the work a pretty full reference book for most of the isolated facts which the student of medicine or pharmacy is supposed to need at some time. From this standpoint the work is deserving of commendation. But the theoretical treatment is by no means as satisfactory ; the student is introduced to a mass of definitions (including a few not very clear paragraphs about ions) before he has learned anything of the preparation or properties of the simpler inorganic substances and compounds, while in the introduction to the subject of organic chemistry we have in the very first pages a discussion of structural formulas, several kinds of isomerism, positive and negative tetrahedra and the difference between maleic and fumaric acids.

There are also a few mistakes in some of these discussions : what is said on page 598 about the optical properties of organic compounds is quite obscure, while the illustrative formula given near the bottom of the page for the calculation of the amount of sugar in a diabetic urine is incorrect. It should be $c = \dfrac{100 \times 1.5}{52.5 \times l}$. On page 593 " Practical Distillation " is written for what is evidently intended to be " Fractional Distillation."

Volume II contains sections on qualitative analysis, quantitative analysis, pharmaceutical assaying, urine analysis, and the examination of water and milk. This work seems to be fairly

well compiled and will doubtless satisfy the needs of those for whom it is intended. The portion devoted to pharmaceutical assaying would be much improved by including the simple and accurate processes of liquid percolation introduced by Hulsebosch and modified by Schwickerath and others, in which the so-called perforator is used.   J. H. LONG.

LABORATORY INSTRUCTIONS IN GENERAL CHEMISTRY. ARRANGED BY ERNEST A. CONGDON. Philadelphia : P. Blakiston's Son & Co. 1901. 110 pp. 8vo. Illus.

The 262 experiments herein described accurately, yet tersely, range from the simplest demonstrations of physical and chemical changes, through the isolation and study of the non-metals (so far as convenient for beginners) up to those dealing with the law of the conservation of matter, the laws of Lavoisier, of Dalton, of Charles, of Boyle, and of Gay-Lussac, and concluding with methods of determining molecular and atomic weights. Throughout the book, the experiments seem to be well graded, carefully chosen, and adequately described ; many are elucidated by illustrations of well arranged apparatus.

The material is largely original, and the author has had ten years' experience in testing his exercises as professor in the Drexel Institute, Philadelphia. The present writer would suggest that the introduction sparingly of stoichiometrical examples might strengthen the educational value of this excellent laboratory guide. The book can be used in connection with any standard text-book. Nearly every experiment is followed by queries intended to make the students think for themselves, and the blank pages with which the book is interleaved furnish opportunities for recording replies, as well as the results obtained.

Students pursuing the course herein outlined, will be well prepared to take up the study of qualitative and quantitative analysis.   HENRY CARRINGTON BOLTON.

AN INTRODUCTION TO MODERN SCIENTIFIC CHEMISTRY, in the form of popular lectures suited for university extension students and general readers. BY LASSAR-COHN. Translated from the second German edition by M. M. PATTISON-MUIR. New York : D. VanNostrand Company. 1901 348 pp. 12mo. Illus. Price, $2.00.

The plan of this book is well conceived and the subject is skilfully presented ; being in the form of popular lectures the style is rather diffuse, though perhaps not more so than necessary for

the comprehension of the class of readers to which the book appeals. The author opens with a discussion of the bearings of physics and of chemistry, and illustrates by describing the distillation of water, and the union of iron with sulphur. We think the definition of chemistry, as given on page 4, rather awkwardly expressed, and liable to the interpretation that it includes, in part, facts that belong to physics.

After making the reader familiar with the practical operations of preparing and examining hydrogen, chlorine, and the other elements of this group, the subjects of atoms and their weights, formulæ, molecules and their weights, and very simple calculations on stoichiometrical principles, are introduced ; this postponement of theoretical questions until after certain phenomena have been studied is advantageous. Then follows the study of oxygen, sulphur, and so on. In the chapter on carbon, the student is gently led into the field of organic chemistry, which is exploited only briefly, yet he becomes acquainted with the classification of hydrocarbons, the signification of isomerism and the '' chemistry of rings.''

In this way, the student insensibly gains some conception of organic chemistry before the term itself is used, and is ready to appreciate the few pages on chemistry of organized substances. Only forty pages are given to metals, and the book closes with an exposition of the periodic law.

A feature of the book is the absence of dogmatic assertions and the continuous introduction of reasoning. Teachers will do well to give the book a trial. The translation bears marks of haste or carelessness. Witness the following phrase : '' That apparatus suffices for quite a few purposes only,'' and the English sentences on several pages. The make-up of the book is excellent ; the illustrations are good, and the index is quite full.

<div align="right">HENRY CARRINGTON BOLTON.</div>

FLESH FOODS : THEIR CHEMICAL, MICROSCOPICAL, AND BACTERIOLOGICAL EXAMINATION. BY C. AINSWORTH MITCHELL. London : Charles Griffin & Co., Ltd. ; Philadelphia : J. B. Lippincott Co. 1900. xv+336 pp.

This book contains nothing really new or which cannot be found elsewhere in scientific literature, but it has the great merit of containing, in condensed form, methods, investigations, and tables which are scattered here and there in scientific works.

According to the preface, '' It has been the author's endeavor to collect and summarize, in a convenient form, records of investi-

gations which are, for the most part, scattered through English
and foreign scientific books and periodicals, and to select such
methods as appeared most suitable for the examination of meat
and its preparations.''

Chapters I and II have to do with the structure and chemical
composition of muscles, tissues, and blood. In Chapter III, the
flesh of animals which are eaten by man, including wild animals,
fish, and birds, is described, giving the general characteristics and
chemical composition. Next the examination of flesh, both
sound and unsound, is taken up, giving methods and chemical
constants. The next chapter summarizes some of the ways
of preserving flesh, as by salting, drying, smoking, and by
use of antiseptics. It includes several tests for antiseptics and
preservatives in meat, and the examination of canned goods. One
chapter is given to the composition and analysis of sausages, and
one to the classification of flesh proteids. The changes due to
cooking and the effects of parasites are well described. About
thirty pages deal with the bacteriological examination of flesh,
describing the principal bacteria which infest flesh, and giving
methods for their detection. It closes by giving the best methods
for the detection and separation of ptomaines.

The author refers freely to such eminent authorities as König,
Chittenden, Hehner, and others.

The attempt has been made to cover such a wide field that it
has been necessary to condense the matter much, but the con-
densation has been done very intelligently.

On the whole, it is a valuable and practical work and will be
found a very useful handbook for analytical chemists.

<div align="right">W. B. BROWN.</div>

A TEXT-BOOK OF URINE ANALYSIS FOR STUDENTS AND PRACTITIONERS
OF MEDICINE. BY JOHN H. LONG, M.S., Sc.D. Easton, Pa.: The
Chemical Publishing Co. 1900. 221 pp. Price, $1.50.

An unusually clear and concise presentation of a well-worn
subject. This manual is not only to be recommended to the stu-
dent of medicine, but equally as well to the chemist and pharma-
cist, who will find it a great aid in the interpretation of analyses
through the numerous references to clinical significance, and the
appended tables, which explain in a very lucid manner the rela-
tion of pathological conditions to chemical composition. An
especially commendable feature is the absence of discussions of

various complicated methods of doubtful value, which crowd many books of this class, much to the confusion of the student. We miss a reference to Howe's modification of Doremus' ureometer, which has added so much to the accuracy and convenience of urea determinations. The illustrations devoted to the microscopical examination of sediments and casts leave room for improvement, both in quality and number. The general make-up of the book is very neat. V. COBLENTZ.

INORGANIC CHEMISTRY. General, Medical and Pharmaceutical, Theoretical and Practical. A text-book and laboratory manual in two volumes. BY OSCAR OLDBERG, PHARM. D. Chicago : Chicago Medical Book Co. 1900. xx + 1177 pp. Price, $7.00.

Volume I is theoretical and descriptive, being divided into three general parts, of which 314 pages are devoted to theoretical chemistry, 150 to the elements and 33 to stoichiometry. Chemical theory is treated in a very thorough and ingenious manner; however, much of this matter could be more readily grasped by the student if classified under the study of the several non-metallic elements. The employment of *approximate* atomic weights, selecting, for example, such values as 120 instead of 120.4 (O = 16) for antimony and 206.5 instead of 206.9 (O = 16) for lead, is not advisable in a text-book of chemistry, for it not only adds to the confusion already existing but also a promiscuous rounding off of these values for convenience sake leads to loose and inaccurate work. The chapter devoted to the periodic system is excellent.

Volume II is more properly a laboratory manual, the first part covering general chemical and pharmaceutical operations, while the second gives working methods for the preparation of 500 pharmaceutical chemicals. No general acknowledgment is made as to the source of the majority of the illustrations.

The work is eminently practical and sufficiently comprehensive to fulfil the requirements of the student and practical pharmacist. The printing and binding is excellent and reflects credit on the publishers. V. COBLENTZ.

HANDBOOK OF PRACTICAL HYGIENE. BY D. H. BERGEY, A.M., M.D. Easton, Pa.: The Chemical Publishing Co. viii + 164 pp. Price, $1.00.

This small work of about 160 pages, to quote the author's preface, is due to "the lack of a convenient handbook for the guidance of students in the sanitary analysis of air, water, soil,

and the principal food materials, and in testing the ventilation of buildings.'' The author confines himself to the simple methods used in the analysis of the substances mentioned.

The book consists of an introduction, five distinct parts, and a complete index. Part I—Atmospheric Air; Part II—Water; Part III—Soil; Part IV—Sanitary Analysis of Foods; Part V—Ventilation and Heating.

No mention is made of microscopic examinations, of waters, or of food products.

"A Brief Outline of the Sanitary Analysis of Water, Air, etc.," would have been a more appropriate title; the one used is very misleading, as the subject of hygiene is only mentioned in the historical introduction.

The book seems to be intended for the use of the medical student and '' may be a means of lightening his labor in this line of study.'' (?)   EDWARD GUDEMAN.

THE CHEMISTS' POCKET MANUAL. BY RICHARD K. MEADE, B.S. Easton, Pa. : The Chemical Publishing Co. 1900. vii+204 pp. Price, $2.00.

This is almost a model work of its kind. Its excellencies are too numerous to mention ; among the important ones are good paper, clear type, convenient shape, strong and handsome binding, on the publisher's side, and accuracy, good style, and clearness on the part of the author.

The contents include almost everything which a chemist or metallurgist would consult it for, the data and methods all fresh and up-to-date. Of particular merit are the graphic methods for saving calculation, composition of standard and special reagent solutions, the valuable collection of special methods of technical analysis and the copious references to recent literature.

It being possible to point out but a few of the excellencies of the work, it is almost unfair to indicate its few shortcomings. It is hardly fair to the chemist who buys the book to tell him to recognize a cyanide by pouring hydrochloric acid on it and smelling the gas! (p. 125). Some of the data are intermixed ; a little rearrangement would improve the first fifty pages. It should also contain, in my opinion, tables of the heats of combinations of salts, specific heats of compounds, the properties and composition of the most common and useful minerals, and a résumé of assay methods. A marking thread would at times be found

useful. I advise every chemist, metallurgist, and assayer to procure the book.

JOSEPH W. RICHARDS.

ANNUAIRE DE L'OBSERVATOIRE MUNICIPAL DE PARIS, DIT OBSERVATOIRE DE MONTSOURIS, POUR L'ANNÉE 1900. Librairie Gauthier-Villars, Paris. 18mo. 563 pp. Price, 2 francs.

The principal work of this observatory is not star-gazing, but a supervision of the hygiene of the city, as a short perusal of this somewhat belated, but yet valuable, yearly report shows. Founded in 1870, its work is now along the following lines : I. Physical and meteorological, including, besides the usual records, a study of atmospheric electricity, of smoke, of the air of the sewers, etc. II. Chemical, comprising the composition of the air in different parts of the city, in schools, public buildings, sewers ; the examination of the water supply, of the Seine water, of the sewer water, and of the subterranean waters in and around Paris ; of the rain, snow and fog ; also sanitary questions submitted by the municipality, as the efficiency of disinfectants, etc. III. The micrographic service makes bacteriological examinations of the air, water, food, drains, sewage, Seine water, soil, and has a special service for contagious diseases.

The thousands of analyses, conveniently tabulated, will be of great interest and value to all concerned in the sanitation of cities or towns. For example, the carbonic acid in the air at Montsouris, taken every day for fifteen years, averaged 30 liters per 100 cubic meters. It is greater in winter than summer ; also greater at night than in daytime at Montsouris, but *vice versa* in Paris.

Altogether, the book is well worth its price, especially to the sanitary chemist. JOSEPH W. RICHARDS.

EXPERIMENTAL PHYSICS. BY EUGENE LOMMEL. Translated by G. W. MYERS from the third German edition. Philadelphia : J. B. Lippincott Co. 1900. xxii + 664 pp.

Eighty-two pages are devoted to motion, 23 to solids, 31 to liquids, 35 to gases, 81 to heat, 17 to magnetism, 56 to electricity, 114 to electrical currents, 47 to waves and sound, 157 to light. This is one of the best text-books on physics that has ever been written, and we have here a very creditable English translation. No book and no translator can hope to avoid all slips and the definition of electromotive force as a quantity of work (p. 334) is

an unfortunate way of putting things, while the spelling of du Bois-Reymond's name on p. 360 and elsewhere must be charged against the translator. Apart from a few similar minor points, the book is phenomenally satisfactory and to be recommended to every one.   WILDER D. BANCROFT.

EVOLUTION OF THE THERMOMETER. BY HENRY CARRINGTON BOLTON. Easton, Pa. : The Chemical Publishing Co. 1900. 98 pp. Price, $1.00.

The period covered is the century and a half between 1592 and 1743. The author defends the view that the first thermometer was due to Galileo. This instrument was an air-thermometer with a liquid seal. The plan of measuring the expansion of a liquid in a sealed tube dates from about 1644 ; in 1664, we find Boyle introducing the idea of a fixed point ; in 1669 we have the suggestion of two fixed points by Honoré Fabri ; in 1694, Renaldini argued in favor of the freezing-point and boiling-point of water as the two fixed points. The mercury thermometer as a practical instrument is due to Fahrenheit, and for years his instruments were the best in the world. The centesimal scale was suggested by Celsius in 1742 ; but it will be news to many people that Celsius took the boiling-point of water as zero, and that the inverted scale, which we call by the name of Celsius, was due to Christin. The book is interesting, the illustrations are curious, and the color of the binding is atrocious.

WILDER D. BANCROFT.

THE CHEMICAL ANALYSIS OF IRON. BY ANDREW A. BLAIR. Fourth edition. Philadelphia : J. B. Lippincott Co. 1901. xi + 319 pp. Price, $4.00.

The new edition of this standard work on iron analysis has been entirely rewritten and a number of recently improved methods have been incorporated. Among the new material are Vanier's modification of Deshays' method for the rapid determination of manganese in steel, Bamber's method for sulphur in pig-iron, the ether methods for the determination of nickel, chromium, and aluminum and, under carbon, there appear a number of new methods and modifications. The ferro-alloys of molybdenum, chromium, silicon, and titanium are given due attention in this edition. Under coal and coke analysis the methods are those reported by the Committee on Coal Analysis of the American Chemical Society.   P. W. SHIMER.

THE JOURNAL

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ON THE ACTION OF ALKYL THIOCYANATES AND ALKYL ISOTHIOCYANATES WITH THIOL ACIDS.

BY HENRY L. WHEELER AND HENRY F. MERRIAM.
Received March 30, 1901.

THE fact that dithiocarbamic esters are formed from alkyl thiocyanates and hydrogen sulphide led Chanlaroff[1] to examine the behavior of ethyl thiocyanate, C_2H_5SCN, with thioacetic acid, thioacetic anhydride, and thiobenzoic acid. He found, in each case, that the compounds reacted and that crystalline products resulted. However, he only described the addition product with thioacetic acid, and to this he assigned the formula $CH_3CONHCS.SC_2H_5$. He remarked, that this addition product behaved like a "molecular-verbindung" and that it showed such great instability in its reactions that all attempts to prepare a derivative from it, of any sort, were without success.

Numerous acyl dithiocarbamates of this type have been prepared by Dr. T. B. Johnson and ourselves, and we have found that derivatives can easily be prepared from the above and also from a large number of other acyldithiourethanes.

Our work has shown that thiocyanates, RSCN, readily react with thiol acids, on the steam-bath, in at least two ways. The

[1] *Ber. d. chem. Ges.*, **15**, 1987 [1882].

more commonly observed reaction is a direct addition as found by Chanlaroff :

$$\text{I. } C_2H_5SCN + HSCOC_6H_5 = C_2H_5S.CSHNCOC_6H_5.$$

Primary monothiocyanates, with aliphatic groups, as well as those prepared from benzyl, p-brom, p-nitrobenzyl, and m-xylyl halides, react almost entirely in this manner and very small amounts of by-product are formed. The di- and polythiocyanates appear to behave in a different manner and work on these is now in progress here.

Certain thiocyanates, even when the action is moderated by heating in the presence of benzene, react in a complicated manner. They evolve hydrogen cyanide and thiol esters result. The action apparently takes place in the following stages :

$$\text{II. } C_6H_5SCN + HS.COC_6H_5 = C_6H_5S.COC_6H_5 + HNCS.$$
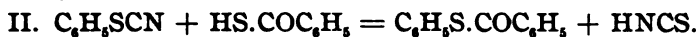
The thiocyanic acid which is liberated then breaks down into hydrogen cyanide and other products.[1] Besides, it has been observed to react with thiobenzoic present in the following manner :

$$\text{III. } HNCS + HS.COC_6H_5 = H_2NCOC_6H_5 + CS_2.$$

The products are carbon disulphide and benzamide and the reaction is similar to that of hydrogen sulphide and thiocyanic acid when ammonia and carbon disulphide are obtained.[2]

In these latter reactions the products are, therefore, thiol esters, benzamide, hydrogen cyanide, and carbon disulphide ; occasionally hydrogen sulphide is noticed, probably as a decomposition product of the thio acid, and in certain cases, especially when the reactions are performed without benzene, the above products are accompanied by thick oils, varnishes, or tars from which it is difficult to isolate anything solid in a state of purity.

The isothiocyanates, RNCS, or mustard oils react even more energetically with thio acids than the normal thiocyanates. When phenyl mustard oil or allyl mustard oil is warmed with thioacetic or thiobenzoic acid, a reaction takes place below the boiling-point of benzene, apparently in a quantitative manner as follows:[3]

$$\text{IV. } RNCS + HS.COC_6H_5 = RNHCOC_6H_5 + CS_2.$$
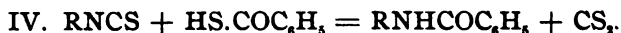
[1] Peter Klason : *J. prakt. Chem.*, [2], 26, 57 (1887).

[2] Voelckel : *Pogg. Ann.*, 65, 313 (1845).

[3] Since the above was written Eibner (*Ber. d. chem. Ges.*, 34, 660) has published the surprising statement that phenyl mustard oil does not react with thioacetic acid on long heating in a tube at 100°. We find that the substances react at ordinary temperature.

This reaction is of the same nature as that of thiocyanic acid with hydrogen sulphide, thiobenzoic acid, etc., mentioned above. It is also analogous to that observed by Kay,[1] who found that phenyl mustard oil and benzoic acid gave carbon oxysulphide and benzanilide, although at a much higher temperature than that in the present experiments.

Not only the alkyl, but also the acyl, isothiocyanates behave in this manner. Benzoyl rhodanide, C_6H_5CONCS, and thiobenzoic acid, for example, gave off carbon disulphide and dibenzamide was isolated and identified.

The above reactions sharply distinguish the thiocyanates from the isothiocyanates, and when a rhodanide is heated with thiobenzoic acid, the non-formation of carbon disulphide may be considered as conclusive proof that an isothiocyanate or mustard oil form is not present. We have now applied these reactions to the examination of some compounds described as mustard oils.

Before entering on the discussion of this it may be well to state that when reactive organic halogen compounds are boiled with potassium thiocyanate, the first product formed appears, in all cases, to be a normal thiocyanate, R—SCN. When the group R is strongly negative[2] the product immediately undergoes a molecular rearrangement into the form RNCS[3] (when R is the group C_6H_5CO—, etc.).

Less negative groups, such as the allyl group,

$$CH_2=CH-CH_2-,$$
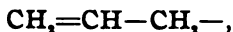
permit of the isolation of the primary product, allyl thiocyanate, if heating is avoided, otherwise allyl mustard oil is obtained. When, in other cases, a halide of the form — CH_2X is employed the thiocyanates show the greatest stability. Methyl thiocyanate is only partially converted into mustard oil on heat-

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[1] *Ber. d. chem. Ges.*, **26**, 2848 (1893).

[2] Miquel : *Ann. chim. phys.*, (5), **11**, 318 (1877) ; Dixon : *J. Chem. Soc.* (London), **75**, 388 (1899).

[3] The mechanism of this reaction or rearrangement appears to the writer to be as yet unexplained. The view accepted at present that the more negative the group, the more readily the rearrangement takes place (compare Michael : *J. prakt. Chem.*, **37**, 510 (1888), requires some modification, since data have already been collected that are not in accordance with this view. We hope to return to this subject at a later date. The methylene dissociation theory of Nef (*Ann. Chem.* (Liebig), **298**, 370 (1897)) does not offer a simple explanation of the rearrangement which, in all probability, takes place in the case of acyl sulphocyanates. An attempt to prepare normal benzoyl thiocyanate, $C_6H_5CO.SCN$, by acting on potassium thiolbenzoate, suspended in benzene, with cyanogen bromide gave benzoyl disulphide as the chief product. W.

ing at a temperature of 180°–185°.[1] Recently, however, a number of cases have been described in which the grouping —COCH$_2$X is said to yield mustard oils directly.

According to Beckurts' and Frerichs,[2] on carefully treating chloracetylethylurethane, ClCH$_2$CONHCO$_2$C$_2$H$_6$, with potassium thiocyanate, a mustard oil derivative is formed ; namely,

SCNCH$_2$CONHCO$_2$C$_2$H$_6$.

The mustard oil structure was assigned to this from the fact that when the compound is treated with alkali and then with hydrochloric acid, hydrogen sulphide is evolved. When this substance is heated it undergoes a molecular rearrangement into what the above authors considered was the normal thiocyanic derivative, but later work showed that the rearranged product was a hydantoïn.[4]

The belief that iso- and normal thiocyanates resulted in this experiment led Frerichs and Beckurts[5] to examine rhodanacetic acid and its derivatives and they claim that none of the salts and esters described by Claësson have the normal form, but that all are derived from isothiocyanic acid. They add that rhodanacetamide prepared from chloracetamide also has the mustard oil structure.

In a later paper, Frerichs and Beckurts[6] state that no normal thiocyanacetic acid exists, and that there are no derivatives of the same. In other words, these compounds are all mustard oils, while according to their last paper[7] rhodanacetanilide has the normal form NCSCH$_2$CONHC$_6$H$_5$, and the perfectly analogous rhodanacetmethylanilidehas the iso structure SCNCH$_2$CONCH$_3$C$_6$H$_5$.

The fact that these compounds give off hydrogen sulphide under the above-named conditions is the only fact, as yet published, on which the iso or mustard oil structure is based. Since we have found that certain compounds of the normal form give off hydrogen sulphide under similar treatment, the beautifully crystallizable benzyl thiocyanate, C$_6$H$_5$CH$_2$SCN, for example, it is at once evident that this reaction cannot be used as a test for isothiocyanates.

We have, therefore, prepared and examined the behavior of all of

[1] Hofmann : *Ber. d. chem. Ges.*, 13, 1350 (1880).
[2] *Arch. d. Pharm.*, 237, 286.
[3] *Ibid.*, 237, 304 (1899).
[4] *Arch. d. Pharm.*, 238, 319 ; *Centrlb.*, 71, (2), 182 (1900).
[5] *Arch. d. Pharm.*, 238, 9 ; *Centrlb.*, 71, (1), 589 (1900).
[6] *Arch. d. Pharm.*, 238, 320 ; *Centrlb.*, 71, (2), 182 (1900).
[7] *Arch. d. Pharm.*, 238, 615 ; *Centrlb.*, 71, (2), 1270 (1900).

the above compounds as well as various analogues with thiobenzoic acid and our results show conclusively that not a single one of these rhodanides has the mustard oil structure. Not only the esters of Claësson have the formulas originally assigned to them, but also the homologous series of rhodanides, recently prepared in this laboratory, are true thiocyanates.[1]

This is shown by the fact that in the reactions with thioben zoic acid, the substances combine to form addition products or acyl dithiourethanes. That not even a trace of a mustard oil is present in these compounds follows from the entire absence of carbon disulphide in the reactions.

As far as the authors are aware it has not been observed that the usual molecular rearrangement of thiocyanates into mustard oils is a reversible reaction. Even were this true, in view of the fact that the mustard oils react with thiol acids more readily than with the thiocyanates, the assumption that in these reactions the compounds undergo a rearrangement into normal forms is excluded.

The results, now at hand, show that *neither isothiocyanacetic acid nor any of its derivatives have yet been prepared.*

In Beilstein's Handbuch[2] the rhodanide which results on boiling 1,2-dichlorpropylene with potassium thiocyanate[3] is listed both under the heading of thiocyanates and of mustard oils. We find, when this product is warmed with thiobenzoic acid, that carbon disulphide is evolved in quantity and that 2-chlorpropylene benzamide, $CH_2=CCl—CH_2NHCOC_6H_5$, is formed. This rhodanide is therefore a mustard oil.

Berthelot[4] states, from thermochemical investigations,[4] that phenyl thiocyanate was observed to be transformed, for the greater part, into isothiocyanate on simply standing during a summer month. Our experiments with this substance do not confirm this statement. We have observed that it remains practically unaltered on keeping at a temperature of $34°–36°$ for four weeks. Perhaps these conflicting results are to be explained by the fact that, in certain cases, a small amount of foreign substance or impurity acts by catalysis and is capable of producing a molecular rear-

[1] Wheeler and Barnes: *Am. Chem. J.*, **24**, 60 (1900).
[2] Vol. I, 1279 and 1283.
[3] Henry: *Ber. d. chem. Ges.*, **5**, 188 (1872) ; *Bull. Soc. Chim.*, (Paris), **39**, 526 (1883).
[4] *Compt. rend.*, **132**, 57 ; *Ann. chim. phys.*, (7), **22**, 327 (1901).

rangement, as in the case of the imido esters and thioncarbamic esters, etc.

The statement of Chanlaroff in regard to the unstable nature of acetyl dithioethylcarbamate would indicate a wide difference between properties of acyl dithiocarbamates and the acyl thioncarbamates ; we find, however, that the two series are closely similar in some respects, and that acylimidodithiocarbonic esters can be obtained from the sodium salts of these carbamates with no greater difficulty than attends the preparation of other imidothiocarbonic esters.[1] The reaction proceeds as follows :

$$\text{V.} \quad CH_3CO-N=C\begin{array}{l}SNa\\SC_2H_5\end{array} + IC_2H_5 =$$

$$CH_3CON=C\begin{array}{l}SC_2H\\SC_2H_5\end{array} + NaI.$$
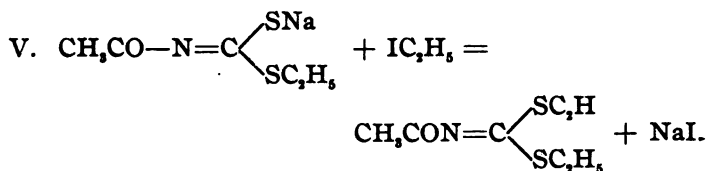
The lower members of this series as well as the corresponding benzoyl derivatives distil unaltered under diminished pressure. In a later paper the results of an examination of these compounds will be more fully given, especially those containing different alkyl groups, since, according to Hantzsch, they should exist in stereoisomeric forms.   When these acylimidodithiocarbonic esters are treated with ammonia and organic bases a new type of pseudo-thioureas result.   The reaction proceeds smoothly in the cold, with evolution of mercaptan as follows :

$$\text{VI.} \quad C_6H_5CON=C\begin{array}{l}SCH_3\\SCH_3\end{array} + HNRR' =$$

$$C_6H_5CON=C\begin{array}{l}NRR'\\SCH_3\end{array} + HSCH_3.$$
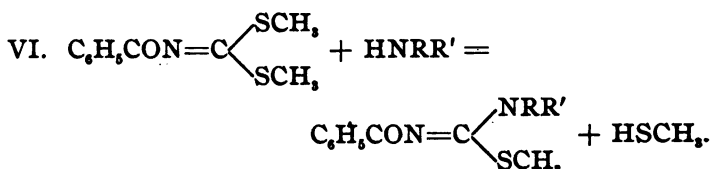
Hitherto only one acylpseudothiourea has been obtained in a state of purity,[2] namely, monoacetylethylisodiphenylthiourea, $C_6H_5N = C(SC_2H_5)N(C_6H_5)COCH_3$; this, however, was prepared by a different method.   It formed a thick oil which could not be crystallized.   The compounds obtained by us differ most decidedly from the oxygen analogues and from the compound of Dains by their great tendency to crystallize and the ease with

[1] Liebermann : Ann. Chem. (Liebig), 207, 141 (188) ; Fromm and Block : Ber. d. chem. Ges., 32, 2210 (1899) ; Busch and Lingenbrink : Ibid., 2620 ; Wheeler, Barnes, Johnson, and Dustin : Am. Chem. J., 24, 60 ; Ibid., 189 ; Ibid., 424 (1900).
[2] Dains : This Journal, 24, 197 (1900).

which they can be purified. A description of their reactions is reserved for a later paper.

As there appear to be no data in the literature in regard to the behavior of acyldithiocarbamic esters with organic bases we have investigated the action of aniline on some of the acetyl and benzoyl derivatives. It was shown in a previous paper[1] that the acylthioncarbamic esters react in an abnormal manner with ammonia and aniline, that hydrogen sulphide was evolved and pseudoureas were formed. An analogous reaction appears to take place with the dithio esters and aniline; inasmuch as hydrogen sulphide is evolved, however, by far the chief products are normal ureas, the behavior being more strictly analogous to that of acetylurethane which was thoroughly investigated by Young and Clark.[2] As a contribution to our knowledge of the saponification of urethanes by aniline we examined also the behavior of benzoylethylcarbamate, $C_6H_5CONHCO_2C_2H_5$. We were unable to detect any signs of the formation of a pseudourea in this case; the chief reaction took place with the formation of benzoylphenylurea and alcohol.

As found by Chanlaroff, ammonia acts on the acyldithiocarbamic esters of the above type; with complete decomposition, mercaptan and ammonium thiocyanate are formed. This reaction is in marked contrast with that of the acylthioncarbamic esters, $C_6H_5CONHCS.OC_2H_5$, for example, which with alcoholic ammonia in the cold, passes quantitatively into benzoylpseudoethylurea,

$$C_6H_5CON{=}C\underset{\textstyle OC_2H_5}{\overset{\textstyle NH_2}{\big<}}$$
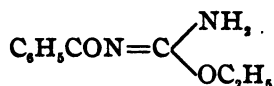
In this connection it is interesting to note that the "imidodicarbonsäuretrithiodibenzyl ester," $C_7H_7S.CONHCS.SC_7H_7$, prepared from phenylmethyldithiomonobenzyldi-c-methylketuret and concentrated hydrochloric acid, according to Fromm and Junius,[3] reacts in the normal manner since monothiobiuret and benzyl mercaptan are formed. We find that a similar normal reaction takes place with the acylthiolcarbamic esters, mercaptan is evolved, and an acylurea is obtained. These three reactions with ammonia are apparently peculiar to the different series of acyl thiocarbamates.

[1] Am. Chem. J., 24, 189 (1900).
[2] J. Chem. Soc. (London), 73, 361 (1898).
[3] Ber. d. chem. Ges., 28, 1105 (1895).

EXPERIMENTAL PART.

The thiocyanates are capable of combining or reacting with thioacetic and thiobenzoic acid at a much lower temperature than that at which Chanlaroff worked. In all cases a smoother reaction is brought about by simply warming a few hours in benzene solution. In certain cases the substances combine at ordinary temperature after long standing. The acyldithiocarbamates thus formed, are all soluble in alkali and most of them can be purified (from disulphide) by precipitating with carbon dioxide. They are converted by a 10 per cent. sodium hydroxide solution, as a rule, into colorless plates of the sodium salts which dissolve on further dilution. The action of alkali, however, produces more or less decomposition into rhodanide and mercaptan, with the formation of thiobenzoic and hydrocyanic salts. They are almost all readily soluble in hot alcohol, but with difficulty in cold, and, like urethanes in general, they form beautiful crystals. They have a yellow color without exception.

Acetyldithiomethyl carbamate, $CH_3CO.NHCS.SCH_3$, is formed practically quantitatively when the constituents are heated dry, or with benzene as a solvent. When crystallized from alcohol it forms long, slender, bright yellow prisms which melt at 119°. A nitrogen determination gave :

	Calculated for $C_4H_7ONS_2$.	Found.
Nitrogen	9.3	9.2

Acetyldithioethyl carbamate is the only one of these carbamates that has hitherto been described. It is formed at ordinary temperatures when the rhodanide and thioacetic acid are allowed to stand for a number of weeks, or almost quantitatively when heated for a short time on the water-bath. It forms long, bright yellow prisms which melt at 123°.

Acetyldithiodiethyl carbonate, $CH_3CON{=}C{\Big\langle}{\begin{matrix} SC_2H_5 \\ SC_2H_5 \end{matrix}}$.—When 22 grams of the above carbamate, 3.1 grams of sodium, dissolved in 125 cc. of alcohol, and 20 grams of ethyl bromide were mixed, a reaction took place in a short time and sodium bromide separated. After standing a number of hours, water was added and the precipitated oil was extracted with ether, washed, dried, and distilled at 14 mm. pressure, whereupon 19.2 grams of colorless oil

were obtained, boiling sharply at 142° (74 per cent. of the calculated). There was no sign of decomposition during the distillation and an analysis of this oil gave :

	Calculated for $C_7H_{13}ONS_2$.	Found.
Nitrogen	7.3	7.6

When this compound is treated with organic bases mercaptan is evolved and pseudothioureas are formed.

Acetyldithionormalpropylcarbamate, $CH_3CONHCS.SC_3H_7$, was prepared from normal propyl rhodanide, boiling at 164° at 761 mm. pressure. This combines smoothly with thioacetic acid and the product crystallizes from dilute alcohol in brilliant yellow plates or flattened prisms melting at 78°. A nitrogen determination gave :

	Calculated for $C_6H_{11}ONS_2$.	Found.
Nitrogen	7.9	7.7

Cetyl thiocyanate, $C_{16}H_{33}SCN$.—Kahlbaum's cetyl iodide (30 grams) readily reacted with potassium thiocyanate in alcoholic solution. The product boiled at 242°–249° at 30 mm. pressure, and at 222° to 227° at 13 mm. pressure. It forms a colorless liquid which, on cooling, solidifies to a white wax. The latter portion of the above distillate, when solidified, showed signs of melting at 12° and then melted at 15°–15.5°. A nitrogen determination gave :

	Calculated for $C_{17}H_{33}NS$.	Found.
Nitrogen	4.94	4.88

Acetylcetyldithiocarbamate, $CH_3CONHCS.SC_{16}H_{33}$.—The above thiocyanate readily combined with thioacetic acid, on warming three or four hours on the steam-bath. It then solidified to a yellow cake of fine radiating crystals. On crystallizing from alcohol it formed a bulky mass of fine hair-like needles which had a lighter yellow color than the lower members of the series, and which melted at 89°–90°. The material dissolved completely in very dilute alkali ; in moderately dilute, it was converted into a mass of colorless, very thin plates of the sodium salt. An analysis gave :

	Calculated for $C_{19}H_{17}ONS_2$.	Found.
Nitrogen	4.13	4.43

Acetyldithiobenzylcarbamate, $CH_3CONHCS.SCH_2C_6H_5$, was

smoothly formed from its constituents. It crystallized from alcohol in bright yellow plates melting at 136°, and a nitrogen determination gave :

	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen..........	6.22	6.50

Benzoyldithiomethylcarbamate, $C_6H_5CONHCS.SCH_3$, is smoothly and apparently quantitatively formed when methyl rhodanide and thiobenzoic acid are warmed for a short time. It forms long, slender, yellow needles melting at 135°, and a nitrogen determination gave :

	Calculated for $C_9H_9ONS_2$.	Found.
Nitrogen........	6.63	6.34

Benzoyldithioethylcarbamate, $C_6H_5CONHCS.SC_2H_5$, is formed as readily as the methyl derivative. It crystallizes from alcohol in stout, yellow prisms melting at 84°. The determination of nitrogen was as follows :

	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen..........	6.22	6.22

Benzoyldithiodimethylcarbamate, $C_6H_5CON=C{<}^{SCH_3}_{SCH_3}$.—Twenty grams of benzoyldithiomethylcarbamate were added to a solution of 2.2 grams of sodium, in methyl alcohol, and then 20 grams of methyl iodide. The mixture, on standing a number of hours, was precipitated with water and the product extracted with ether. On evaporating the ether, after drying, long colorless prisms separated which after crystallizing from dilute alcohol melted at 46°. Yield about 15 grams.

	Calculated for $C_{10}H_{11}ONS_2$	Found.
Nitrogen..........	6.22	6.26

Benzoyldithiodiethylcarbamate, prepared in a similar manner to the above, proved to be an oil, boiling at 220°–221° at 17 mm. pressure. Ten grams of the urethane gave about 6 grams of the oil, and, on analysis, the following per cent. of nitrogen was obtained :

	Calculated for $C_{12}H_{15}CONS_2$.	Found.
Nitrogen..........	5.53	5.88

Benzoylpseudomethylthiourea, $C_6H_5CO-N=C\begin{smallmatrix}NH_2\\SCH_3\end{smallmatrix}$.— When
4.7 grams of benzoyldithiodimethyl carbamate were dissolved in
an excess of alcoholic ammonia and allowed to stand for two days,
mercaptan separated, and, on evaporating the alcohol and crys-
tallizing the residue from a mixture of benzene and ligroin, about
2 or 3 grams of material melting at 111°–112° were obtained. A
nitrogen determination gave:

	Calculated for C$_9$H$_{10}$ON$_2$S.	Found.
Nitrogen	14.43	14.53

Benzoylpseudomethylphenylthiourea, $C_6H_5CON=C\begin{smallmatrix}NHC_6H_5\\SCH_3\end{smallmatrix}$,
was prepared by warming the above dimethyl carbamate, on the
water-bath, with aniline. It forms thin colorless plates from
alcohol, which melt at 104°–105°.

	Calculated for C$_{15}$H$_{14}$ON$_2$S.	Found.
Nitrogen	10.37	10.57

Benzoylpseudoethylphenylthiourea, prepared from the above di-
ethyl carbamate by warming with aniline, formed long colorless
prisms from alcohol which melted at 87°–88°.

	Calculated for C$_{16}$H$_{16}$ON$_2$S.	Found.
Nitrogen	9.85	9.84

Benzoyldithionormalpropylcarbamate, $C_6H_5CONHCS.SC_3H_7$, is
formed as readily as the above dithioethyl carbamate. It crys-
tallizes in bright yellow prisms from alcohol, and it melts at 77°.
A nitrogen determination gave:

	Calculated for C$_{11}$H$_{13}$ONS$_2$.	Found.
Nitrogen	5.85	5.81

Benzoyldithioisobutylcarbamate, $C_6H_5CONHCS.SC_4H_9$. — This
forms transparent golden yellow needles, some over an inch in
length, when prepared from isobutylthiocyanate boiling at 178°–
180°. It melts at 80°–81°, and an analysis gave:

	Calculated for C$_{12}$H$_{15}$ONS$_2$.	Found.
Nitrogen	5.53	5.53

Benzoyldithiocetylcarbamate, $C_6H_5CONHCS.SC_{16}H_{33}$, was

formed as smoothly as its lower homologues.   It forms a beautiful mass of shining, bright yellow plates, when crystallized from alcohol, and it melts at $63°$–$64°$.   A nitrogen determination gave:

	Calculated for $C_{24}H_{20}ONS_2$.	Found.
Nitrogen	3.32	3.30

Benzyl Thiocyanate, $C_6H_5CH_2SCN$.—The melting-point of this compound is given by Henry[1] as $36°$–$38°$, and by Barbaglia[2] as $41°$.   A portion prepared from benzyl chloride and potassium thiocyanate was crystallized several times from absolute alcohol ; it then melted at $43°$–$43.5°$.   A portion of this was treated with dilute sodium hydroxide, and on adding acid then, after warming, or on letting the material stand, hydrogen sulphide was given off.   This was easily recognized by its odor and the black color it gave with lead acetate paper.

Benzoyldithiobenzylcarbamate, $C_6H_5CONHCS.SCH_2C_6H_5$,   results smoothly when the constituents are warmed in benzene solution.   No hydrogen cyanide or carbon disulphide is formed in this case.   When crystallized from alcohol it forms long yellow needles melting sharply at $108°$.   A nitrogen determination gave:

	Calculated for $C_{15}H_{13}ONS_2$.	Found.
Nitrogen	4.87	4.92

This compound gives a difficultly soluble sodium salt which separates from aqueous alkali in colorless, thin plates.   It is readily soluble in alcohol and it is one of the most stable salts of this series, although warm alkali rapidly decomposes it.

Phenyl Thiocyanate, C_6H_5SCN, *and Thiobenzoic Acid*.—The thiocyanate, in this case, was freshly prepared by the method of Gattermann and Hausknecht.[3]   It was allowed to digest, on the water-bath, with thiobenzoic acid for two or three days, whereupon, on cooling, a mass of crystals separated.   This material contained no nitrogen and it proved to be identical with *phenyl thiolbenzoate*, $C_6H_5CO.SC_6H_5$, described by Schiller and Otto,[4] and which melts at $56°$.

A portion of this thiocyanate (7.8 grams) was allowed to stand at $34°$–$36°$ for twenty-eight days, whereupon it was heated with thiobenzoic acid in benzene (20 cc.) for two hours and a

[1] *Ber. d. chem. Ges.*, **2**, 637 (1869).
[2] *Ibid.*, **5**, 689 (1872).
[3] *Ibid.*, **23**, 739 (1890).
[4] *Ibid.*, **9**, 1635 (1876).

half. The benzene was then distilled off and found to contain some hydrogen cyanide and a small amount of carbon disulphide. On cooling, nothing solid was obtained, and no solid was separated by adding ether (absence of notable quantities of benzanilide). In fact, it was found that a large portion of the rhodanide had remained unaltered in this treatment. Unaltered thiobenzoic acid was removed by alkali, and on evaporating the ether solution, nothing but phenyl thiolbenzoate was obtained. The quantity of benzanilide, if formed at all, was insignificant. These results show that phenyl thiocyanate does not readily undergo a molecular rearrangement into phenyl mustard oil, although Berthelot states, from the results of his thermochemical investigations[1] that the thiocyanate was transformed, for the greater part, on simply standing during a summer month.

2,4-Dinitrophenyl Thiocyanate, $C_6H_3(NO_2)_2SCN$, *and Thioacetic Acid*, when heated together, gave a product insoluble in ether, benzene, and alcohol. From nitrobenzene it crystallized in small yellow pyramids which had no definite melting-point; at 250° it began to decompose and was not completely melted at 280°. It was insoluble in alkali. Although a nitrogen determination agreed with the calculated for a dithiocarbamate, the properties of the substance, however, show that this is *tetranitrophenyldisulphide*, $(C_6H_3(NO_2)_2S-)_2$, which has been described by Willgerodt.[2] The nitrogen determination was as follows:

	Calculated for $(C_6H_3(NO_2)_2S-)_2 = C_{12}H_6O_8N_4S_2.$	Found.
Nitrogen	14.0	14.2

When this substance is heated on platinum it explodes.

2,4-Dinitrophenyl Thiocyanate and Thiobenzoic Acid were heated together on the water-bath without benzene. A violent evolution of gas took place which was allowed to pass through water; this then responded to the Prussian-blue test for hydrogen cyanide but gave no test for thiocyanic acid. On crystallizing the residue from 95 per cent. alcohol, plates were obtained which melted at about 100°. This material proved to be impure *benzoyldinitrothiophenol*, which is said to melt at 113° (Willgerodt) or at 111°.[3] On treating this with alkali and then adding acid, the above-mentioned *tetranitrophenyldisulphide* was obtained.

[1] *Loc. cit.*
[2] Beilstein's "Handbuch," **2,** 816; compare *Ber. d. chem. Ges.,* **9,** 978, and **10,** 1686 (1877).
[3] Kym: *Ber. d. chem. Ges.,* **32,** 3532 (1899).

Rhodanacetylethylurethane and Thiobenzoic Acid.—If rhodan-acetylethylurethane has a mustard oil structure it should act with thiobenzoic acid with the formation of hippurylurethane and carbon disulphide. Instead of this, the action took an entirely different course. 5.7 grams of the rhodanide, prepared according to the directions of Frerichs, and melting at 86°, were dissolved in 45 cc. of benzene, and 4.2 grams of thiobenzoic acid were added. The mixture was heated on the water-bath for eight hours, with a return condenser, whereupon a portion of the benzene was distilled off and tested for carbon disulphide, by adding an alcoholic solution of potassium hydroxide. No precipitate of potassium xanthate was obtained, and on adding copper sulphate solution no yellow precipitate resulted. The reaction product was therefore free from carbon disulphide. The alkaline solution gave the Prussian blue test for hydrogen cyanide. The benzene solution was filtered from a small amount of material and, on cooling, minute yellow crystals separated. These formed the chief product of the reaction. When these were crystallized from alcohol thin, golden yellow plates were obtained, which melted at 159°. The color and the following analysis show that this substance is *benzoyldithiocarbamicacetylethylurethane,*

$$C_6H_5CONHCS.SCH_2CONHCO_2C_2H_5:$$

	Calculated for $C_{13}H_{14}O_4N_2S_2$.	Found.
Nitrogen	8.58	8.50

Rhodanacetylethylurethane, therefore, has the structure

$$NCS.CH_2CONHCO_2C_2H_5.$$

Rhodanmethyl Acetate and Thiobenzoic Acid.—The action of the thiocyanic esters of acetic acid with thiol acids is well represented by rhodanmethyl acetate. The behavior of this alone is described here since that of others as well as certain homologues have been used in other work and will be described in a later paper. When the rhodanide in question was warmed with thiobenzoic acid no carbon disulphide resulted and no methyl hippurate was obtained. Thirteen grams of thiobenzoic acid and 12 grams of rhodanmethyl acetate were diluted with 30 cc. of benzene and heated to boiling for six hours. On evaporating off the benzene and crystallizing from alcohol, 14 grams of bright yellow prisms melting at 118° were easily obtained. The properties of the substance and the following nitro-

gen determination show that this is *benzoyldithiocarbamicmethyl acetate*, $C_6H_5CONHCS.SCH_2CO_2CH_3$:

	⁻Calculated for $C_{11}H_{11}O_2NS_2$.	Found.
Nitrogen	5.24	5.65

In the process of formation of the above, traces of hydrogen cyanide are evolved, but otherwise, there appears to be very little by-products formed. It follows, therefore, that rhodanmethyl acetate is a derivative of normal thiocyanic acid and not a mustard oil.

Rhodanacetamide and Thiobenzoic acid, on heating together in benzene solution, evolved hydrogen cyanide and on cooling benzoyldisulphide separated in quantity. On distilling off the benzene and testing for carbon disulphide none was found. This fact establishes that rhodanacetamide is not a mustard oil. The remaining material in the benzene solution was not obtained in a state of purity. It formed a black tar.

Benzoylthioglycollamide, $C_6H_5COSCH_2CONH_2$.—This was prepared from potassium thiolbenzoate and chloracetamide, in order to compare it with the products in the above experiment. It crystallizes from hot water in long colorless prisms which melt at 119°–120°. A nitrogen determination gave:

	Calculated for $C_9H_9O_2NS$.	Found.
Nitrogen	7.18	7.35

Rhodanacetmethylanilide and Thiobenzoic Acid. —When 6.6 grams of this rhodanide and 4.4 grams of thiobenzoic acid with 35 cc. benzene were heated for five hours on the water-bath, no carbon disulphide was formed and nothing corresponding to hippurmethylanilide was obtained. The Prussian blue test showed the presence of hydrogen cyanide and on evaporating off the benzene a tar was found. On treating this with ether and on crystallizing the solid which separated from dilute alcohol yellow, flattened prisms or tables were obtained, which melted at 152° (0.2–0.3 gram). A nitrogen determination agreed with the calculated for *benzoyldithiocarbamicmethylacetanilide*,

$$C_6H_5CONHCS.SCH_2CON(CH_3)C_6H_5 :$$

	Calculated for $C_{17}H_{16}O_2N_2S_2$.	Found.
Nitrogen	8.13	8.08

The above results show that rhodanacetmethylanilide is a derivative of normal and not isothiocyanic acid.

Allyl Isothiocyanate, C_3H_5NCS, *and Thiobenzoic Acid* react immediately on gently warming, carbon disulphide streams off and the remaining light yellow colored oil distils almost entirely from 175°–176° at 14 mm. pressure. Kay[1] gives the boiling-point of *allylbenzamide* as 173°–174° at 14 mm. pressure. The carbon disulphide evolved in these reactions is pure and it has no disagreeable odor, but suggests somewhat that of ether. That it is carbon disulphide was shown in each case by the xanthate test.

Phenyl Isothiocyanate, C_6H_5NCS, *and Thiobenzoic Acid* reacted very readily on the steam-bath; carbon disulphide was evolved and the residue solidified. On crystallizing from alcohol large plates of *benzanilide* melting at 161° were obtained.

Phenyl Isothiocyanate and Thioacetic Acid on standing at ordinary temperatures for a month deposited a mass of colorless plates of acetanilide melting at 114°.

α-Chlorallyl Isothiocyanate, $CH_2{=}CCl{-}CH_2NCS$, *and Thiobenzoic Acid.*—The isothiocyanate was prepared according to the directions of Henry and 5 grams of this were heated with 5.2 grams of thiobenzoic acid in 45 cc. of benzene. After six hours a portion of the benzene was distilled off and this gave an abundant precipitate of xanthate with alcoholic potassium hydroxide. No hydrogen cyanide could be detected. The reaction product was boiled with water to remove some oil and then crystallized from a mixture of benzene and petroleum ether whereupon it was obtained in long colorless flattened prisms melting at 95°. A nitrogen determination agreed with the calculated for *2-chlorallylbenzamide*, $C_6H_5CONHCH_2{-}CCl{=}CH_2$:

	Calculated for $C_{10}H_{10}NCl$.	Found.
Nitrogen	7.17	7.31

Benzoyl Rhodanide, C_6H_5CONCS, *and Thiobenzoic Acid* were warmed for a short time on the water-bath, carbon disulphide was given off, and the residue was treated with alkali and ether (to remove some benzonitrile). The alkaline solution on acidifying gave a product which, on crystallizing from dilute alcohol, formed needles melting at 148°. This material was, therefore, *dibenzamide*.

[1] *Loc. cit.*

Ethyl Selenocyanide, C₂H₅SeCN.—This compound, which appears to be new, was prepared from 16.1 grams of potassium seleno-cyanide and 15 grams of ethyl bromide in alcohol solution. The reaction is complete in a few minutes, and it is best then to add water without distilling off the alcohol. The oil is somewhat volatile in alcohol vapor and also in that of ether. On distilling at 741 mm. pressure it practically all boiled at 172°. It formed a pale yellow oil with a highly disagreeable odor. A nitrogen determination gave :

	Calculated for C₃H₅NSe.	Found.
Nitrogen	10.44	10.38

When this was warmed with thiobenzoic acid it gave off a gas or vapor, with the odor of hydrogen cyanide, and an oil and a solid were obtained. These products were not investigated.

AN IMPROVED METHOD FOR THE RAPID ESTIMATION OF SUGAR IN BEETS.

BY R. S. HILTNER AND R. W. THATCHER.

INTRODUCTION.

EXPERIENCE has abundantly shown that both the good and the bad properties of any individual beet are largely heredi-tary and may be transmitted to succeeding generations of beets. The success of the beet-sugar industry in recent times has been due to a very large extent to the building up of a race of high-grade beets by means of the selection of individual beets having high sugar content for the pro-duction of the seed for later use. Long-continued and care-ful efforts in this direction have resulted in the production of beets of highly satisfactory sugar-producing qualities. This condition is more or less abnormal, however, and the ten-dency is toward a retrogression or reversion to the original state. In order to prevent this and to maintain the present high state of perfection, constant care in the selection of only the best beets for mothers for seed production is necessary. Not only is it essential to select those beets which possess the best form of leaves and root, but care must also be taken that only those whose roots are of high sugar content are used. The sugar content of indi-vidual beet roots under the same conditions of growth varies

widely. It is obvious, therefore, that a knowledge of the sugar content of each beet which is selected is of the utmost importance. The necessity of some simple, rapid, and accurate method for testing small samples taken from individual beets is therefore apparent. Moreover, the rapid development of the beet sugar industry in this country of late, emphasizes the need of some such rapid method adapted to factory control.

DISCUSSION OF PRESENT METHODS.

Many of the methods already suggested for the determination of sugar in beets are very satisfactory as far as accuracy is concerned, but all are more or less complicated and require the use of expensive apparatus and great care in manipulation. Furthermore, a large force of laboratory assistants is necessary in order to make the process of any of the known methods of analysis rapid enough for control work in the selection of mother beets. Dr. François Sachs, of Brussels, Belgium, in a paper read before the second International Congress of Applied Chemistry held in Paris, July 27 to August 5, 1896, gives a very clear and concise statement of the present methods for the analysis of sugar beets and suggests certain modifications and improvements in them. Inasmuch as this article has not yet appeared in American chemical literature, we quote the more pertinent portions of it below:[1]

"We may divide the methods which have been proposed, for this purpose, into three groups:

" 1. The indirect methods based upon the analysis of the juice.

" 2. The alcoholic methods.

" 3. The aqueous methods.

"The indirect methods no longer have any more than an historic interest, and their use, particularly in France, is gradually disappearing, more rational methods taking their place.

" It has long been believed that the use of alcohol is indispensable for the exact determination of the percentage of sugar contained in the beets. Even to-day this appears to be the opinion held by most German sugar chemists. In fact, when one removes the pulp of the sugar beet, extracts with alcohol, and washes the exhausted pulp with water, the aqueous solution thus obtained turns a ray of polarized light distinctly to the right. Hence, it has been concluded that alcohol is necessary to perfect

[1] Translation made by Division of Chemistry, Department of Agriculture, Washington, D. C.

the solution of optically active bodies, such as sugar. But it has been demonstrated, notably by the work of two Belgian chemists, Chevron and Droixhe, that the precipitation of these active bodies (which appear to be pectic bodies) is complete when sub-acetate of lead is added to their aqueous solution.

" It is necessary to conclude, after what has been said, that the alcohol and aqueous methods ought to give the same results with the same beets. This is exactly what has been observed by Pellet, Petermann, Weisberg, and others. The objection has been made that Petermann did not obtain in all of his experiments absolutely identical results, but the differences are so small that they may well be attributed to errors in sampling. Moreover, subsequent experiments made with greater care have given results still more concordant. It may seem that the results obtained by the aqueous diffusion method are too high by about 0.1 per cent., because the hydration of the marc is not taken into account, but this same error must occur when the alcoholic diffusion methods are used.

" On the other hand, the results obtained by the cold aqueous diffusion methods may be too high if the analyst neglects to com-pletely eliminate the air imprisoned in the fine pulp, as has been frequently observed, notably by Woijcki in Russia, and by Nassou at Gembloux. When all of the common errors are elimi-nated, in the application of the two methods, no sensible differ-ence between the results have been observed, either in Belgium or in France. In Germany, on the contrary, most of the chemists generally continue to affirm that the alcoholic methods give more exact results than the aqueous methods, and that for certain abnormal beets the differences may be very considerable.

" I shall not stop to discuss the hot aqueous diffusion methods which give good results, but which have not the desired sim-plicity. The cold aqueous diffusion, designed by our colleague, M. Pellet, is much more practical. However, as has already been said, this method as it is generally applied requires the complete elimination of the air imprisoned in the pulp, and therefore demands especial care. Moreover, the introduction of the pulp by means of a funnel into a flask with a more or less narrow neck, is an operation which it is very desirable to dispense with.

" It is these considerations that led us to modify the ordinaryl methods by introducing the pulp into a large ungraduated vesse

and adding to it at once by means of a pipette, the proper quan-
tity of lead subacetate and water. This method was announced
two years ago (April 24, 1894) at the meeting of the Association
of Belgian Chemists. We then incorrectly attributed the origi-
nal idea to Woijcki. We wish to say now that it should be
credited to Kaiser and Lewenberg.

" Kaiser[1] proposed to use 26.048 grams of the finely rasped
pulp with the addition of 76 cc. of water and lead subacetate
solution. He used a special correction in the case of very rich
beets.

" Lewenberg[2] directed the use of 26.048 grams of the finely
rasped pulp, 3 cc. of lead subacetate and 73.8 cc. of water.

"Woijicki[3] designed a simple apparatus, by means of which he
demonstrated that in the ordinary method even as much as 3.1
cc. of air is left in the flask.

" Walawski[4] proposed to take any convenient weighed quantity
of the beet pulp and to add to it 3.6 times its weight of water and
lead subacetate solution. This modification does not appear
to us to be a desirable one.

" We have in our turn simplified somewhat the form of the
apparatus used. We have found it convenient to use for the
normal weight, 26.048 grams of the beet pulp, about 5 cc. of
lead subacetate solution, and a sufficient quantity of water to
bring the total volume of the liquid contained in the pipette to
77 cc. We tried this method and the results were not satis-
factory. We found that it was necessary to shake the mixture
for a very long time in order to obtain a complete distribution of
the sugar throughout. We then decided to modify the method
more radically and for that purpose constructed a pipette, having
a capacity of 177 cc., which enabled us to obtain the conditions
recommended for the ordinary method. Working in this manner
we obtained perfectly satisfactory results. We have never found
that more than three minutes are necessary to obtain a complete
distribution of the sugar throughout the mixture.''

OBJECTIONS TO PRESENT METHODS.

Any of the methods now in use will give fairly accurate and

[1] *Deutsche Zuckerindustrie*, 1893, p. 413.
[2] Dodatek, 1892.
[3] *Gazeta Cukrowiczna*, 1893, p. 313; *Oester. Zeitschrift*, 1894, p. 146.
[4] *Gazeta Cukrowiczna*, 1894, p. 268; *Oester. Zeitschrift*, 1895, p. 1117.

satisfactory results if carefully carried out. They all possess in general, however, certain inherent sources of error, the inaccuracies resulting from which become greater and greater as carefulness of manipulation is sacrificed to speed. The several sources of error which may be mentioned here are as follows: First, the pulp itself is susceptible to changes in composition during weighing, both through the evaporation of its water and through pressure exerted by the appliances used in transferring the pulp from the dish containing it to the weighing capsule. In rapid work, where pincers or some similar appliance must be used to transfer small portions of the pulp either to or from the weighing dish in order to obtain the exact normal weight, the change in composition of the pulp thus handled becomes quite significant. Moreover, as in all cases where only a portion of the sample is used for analysis (the normal weight or some fraction or multiple thereof), unless great care is taken the portion which is weighed out does not accurately represent an average of the whole sample. Second, the amount of lead subacetate to be used in clarifying the juice varies, and too much or too little of the reagent is liable to be added, with a resulting effect upon the polarization value of the solution. Third, the sample of pulp occupies some space in the flask and the flask does not, therefore, contain exactly 100 cc. of liquid (*i. e.*, sugar solution). This error is compensated for in most cases by using flasks which are graduated at 101.3 cc., the 1.3 cc. additional being adopted as the average value for the volume occupied by the pulp. This requires, of course, specially constructed flasks, and the figure thus arbitrarily adopted is more or less far from the truth in individual cases. Fifth, as has been noted in the article quoted above, the pulp mechanically encloses considerable air, and the error due to the change in volume of solution thus produced may in some cases become very significant. Finally, the volume to which the solution is made is always measured in graduated flasks, the calibration of which is not always accurately done.

Moreover, in all the present methods of analysis as employed in this country, there are certain steps in the process which require considerable care and the manipulation of which requires much time. These interfere seriously with rapid work, and the speed of the operation is consequently quite limited. In the first place, a certain definite weight of pulp must be obtained. If

this is done with a tolerablê degree of exactness considerable
time is consumed.   Next, the pulp must be transferred to a flask
having a somewhat narrow neck.   Owing to the tendency of the
particles of pulp to agglomerate, this is a difficult and tedious
operation at best.   In the third place, the volume of the solu-
tion must be made up to the mark on the neck of the flask with
care.   Since all aqueous solutions of beet juice froth badly while
the water is being added, some precaution to break this froth is
generally necessary and it is with difficulty that the process
is carried out quickly.

An ideal method for the rapid determination of sugar in samples
of beet pulp would, therefore, be one in which the entire sample
as received from the drill would be used, the pulp itself would
not be transferred from the dish into which it is first received,
and the proportion of lead subacetate to the amount of pulp used
would be constant.   The article quoted above describes the recent
attempts by European chemists to modify Pellet's method in ,
order to conform more closely to these conditions.   The modi-
fications suggested obviate some of the objectionable features of
the original method, but give more or less unsatisfactory results.
In order to ascertain and to eliminate, if possible, the sources of
error in the methods suggested by Dr. Sachs, and in order to
take advantage of the more desirable features of these methods,
the present work was undertaken.

THE PROPOSED METHOD.   THEORETICAL CONSIDERATIONS.

In the following discussion the factors required by the Schmidt
and Haensch polariscope are used exclusively.   The principles
involved are general, however, and the method of analysis ,may
be used with any other make of instrument, the factors being
changed accordingly.

It is evident that, in order that the scale of the instru-
ment shall correctly show the percentage of sugar in the
sample taken, a certain relation of weight of pulp taken to volume
of solution must always be maintained; namely, 26.048 : 100.   It
is not necessary that the weight taken shall always be 26.048
grams.   It may be any fraction or any multiple of this, but the
volume of solution must be correspondingly decreased or increased,
and the flask in which the solution is made up to volume must
be calibrated accordingly.   Hence, all methods of analysis now

in use require that the weight of pulp to be taken shall be some simple multiple or fraction of the normal weight, in order that the required volume may be 200 cc., 100 cc., or 50 cc., these being the volumes at which flasks are usually graduated. The 100 cc. of liquid in the solution required by the normal weight of pulp is made up of two components, namely, the water originally present in the juice of the sample and the water added to complete the proper volume. If, now, the quantity of water in the pulp be known, the residual quantity which must be added to give the correct volume of solution, can easily be determined. This amount of water may then be added directly to the pulp in the containing vessel and the necessity for transferring the pulp to a graduated flask and adding water to the mark be obviated. Furthermore, there would then be no necessity for taking just the normal weight of pulp or an even multiple or fraction thereof, since it is only necessary to preserve the ratio of weight to volume mentioned (that is, 26.048 : 100 or 1 gram : 3.839 cc.) in order to preserve the conditions required by the polariscope. In other words, any weight of pulp might be taken and sufficient water added to complete the volume of the solution in cubic centimeters to 3.839 times the weight of the pulp taken.

Not all beets contain the same percentage of water. It is a well-known fact, however, that in general this percentage does not vary through very wide limits. In most cases as the percentage of sugar in the beet increases the percentage of non-sugars decreases, or in other words the total solid matter in the beet does not change as rapidly as does the sugar content. A long series of determinations made at this Station during several years shows that for beets of from 8 per cent. to 15 per cent. sugar content the water content almost always falls between 80 per cent. and 84.5 per cent. Since such wide limits of sugar content, as those mentioned, would include most beets to be analyzed during any season or during a particular period of analysis, it would be possible to assume an average factor for water content which would vary from the true amount of water in any individual beet by not more than 2 per cent., except in very rare cases. A simple calculation will show that this maximum of error in the water factor will not change the dilution of the sugar solution sufficiently to cause a perceptible difference in the polariscopic reading. For example, 2 per cent. of 26.048 equals 0.52.

An error of 2 per cent. in the assumed water factor would then result in the addition of 0.52 gram, or cubic centimeters of water too much or too little. The resulting volume will therefore be 100 ± 0.52 cc., or it will be increased or decreased by 0.52 per cent. of itself, and the polariscopic reading will be correspondingly affected. A beet which should give a polariscopic reading of 14 will therefore read 0.52 per cent. of 14, or 0.07, too high or too low, an error scarcely appreciable in any ordinary polariscope. If in exceptional cases the error in the water factor should rise to 4 per cent. or even to 5 per cent., the corresponding error in the polariscopic reading would amount to less than 0.2 per cent., or in other words an extraordinarily poor beet having an unusually high percentage of water will give a reading slightly too low, or an exceptionally good beet may give a reading slightly too high, but in no possible case would the error due to this cause amount to more than 0.2. In analyses for the selection of mother beets it is customary to double the dilution in order to obtain a larger filtrate from a small sample of pulp, and then double the polariscopic reading. In case this should be done, the possible error due to variation of water content from the factor assumed would be diminished one-half, and in no possible case could there be an error amounting to 0.1 from this source.

It is possible, then, to assume a factor for the water content which will represent the true amount of water present in the beet so closely as to produce no appreciable error in the polariscope reading. If we represent this factor by x, the ratio of weight of pulp taken to the volume of water necessary to be added in order to bring the total volume up to the proper amount would be represented by 26.048 : 100—26.048 x. Having assumed, then, a value for x, this ratio may readily be calculated, and a table arranged to show the exact volume of water to be added to any given weight of pulp in order to bring the total water of the mass up to the correct volume for that weight. For example, if we assume 82 per cent. as this factor, the formula would then become 26.048 : 100—(26.048 × 0.82), or 26.048 : 78.64, or 1 : 3.019. Upon this basis, then, the volume of water to be added in any particular case would be 3.019 times the weight of pulp taken. A table could then be prepared showing the amount of water to be added for any particular weight of pulp taken. In case the samples are to be obtained by means of a boring rasp,

as recommended below, this table would not need to extend over more than 10 grams, between the limits of 5 and 15 grams, since all the samples obtained by the boring rasp will usually fall between these limits of weight. The following arrangement of the table has been found to be very satisfactory :

Grams.→	5	6	7	8	9	10 etc.
	cc.	cc.	cc.	cc.	cc.	cc.
0.00	15.10	18.12	21.14	24.16	27.18	30.20
0.02	15.16	18.18	21.20	24.22	27.24	30.26
0.04	15.22	18.24	21.26	24.28	27.30	30.32
0.06	15.28	18.30	21.32	24.34	27.36	30.38
0.08	15.34	18.36	21.38	24.40	27.42	30.44
0.10	15.40	18.42	21.44	24.46	27.48	30.50
etc.						

Such a table will show at a glance the desired volume to be added. For example, 5 grams of pulp would require the addition of 15.10 cc. of water ; 9.08 grams would require 27.42 cc., etc.

DETERMINATION OF AVERAGE WATER CONTENT.

For the purpose of obtaining figures from which to decide upon the number to be assumed as the water factor in calculating the quantity of water to be added to the pulp, a direct determination by taking samples from as many beets as possible should be made. The beets taken for this purpose should be of as widely different character and grown under as different conditions as are those which are subsequently to be analyzed by this process. A convenient method for determining the water content is as follows : The beet should be split in half longitudinally, and thin slices cut from one of the exposed surfaces from various parts of the beet until about 15 grams are obtained. These thin slices should be received on a weighed watch-glass or other similar dish, covered to prevent evaporation, and their weight immediately determined. The watch-glass should then be placed in a water oven and dried until the loss in weight in one hour is not more than 5 milligrams. From the total loss in weight the percentage of water originally contained may be calculated.

A simple determination of the total solid matter in the juice of the beet by the ordinary method, using a Brix spindle and calculating this value back to that for the original beet by means of the usual coefficient for marc, will not suffice if an accurate

result be required.   Variations in the relative amounts of insoluble solids (marc) are too great.   Furthermore, the fact that the Brix spindle is calibrated in solutions of pure sugar gives rise to an error which has been found to amount to as much as 1½ per cent. in some cases, and its reading is nearly always from 0.5 to 0.8 higher than the figure obtained by a direct determination of the total solids in the juice.

During the investigations upon the applicability of the proposed method made at this laboratory this season, the actual water content of some sixty beets was determined.   These beets were taken from fields in five different sections of the state, and from each field beets of widely different appearance were selected. The following table shows the results of these determinations :

TABLE I.   WATER CONTENT OF BEETS.

Sugar in beet. Per cent.	Number of analyses.	Water content.		
		Maximum. Per cent.	Minimum. Per cent.	Average. Per cent.
8 to 10	11	86.04	82.72	84.64
10 to 12	30	85.22	80.56	83.05
12 to 14	13	83.63	79.91	82.10
Above 14	1	....	....	81.25
Not determined	6	85.16	80.54	82.69
Total, 61			Average, 82.74	

That the above results represent closely the normal condition of beets for any year and that the water content, to a very striking degree, is independent of the season, of weather, and of the kind of cultivation, is shown in the following table.   These data were compiled from results obtained at the Nebraska Experiment Station.   Excepting for the year 1898, the samples analyzed were taken from fields on the Station farm.   Each year the beets were grown in a different field.   The character of the soil in these fields differs considerably.   Moreover the meteorological records for these successive years show a decided lack of uniformity in climatic conditions.   The figures given for 1898 represent the composition of mature beets grown that year at Ames, Nebraska, where the character of the soil, the rain-fall, etc., are wholly different from that at Lincoln.

TABLE II.

Year.	No. of analyses.	Sugar in beet.			Percentage of water.		
		Max.	Min.	Average.	Max.	Min.	Average.
1892	9	14.2	10.8	12.7	83.70	80.75	81.74
1894	7	13.8	10.6	11.9	83.66	80.24	82.00
1895	9	10.3	7.3	8.6	85.64	83.64	84.51
1896	5	13.5	11.1	11.8	84.14	82.11	83.27
1897	10	13.8	10.8	12.3	85.65	80.26	81.89
1898	9	15.5	11.8	13.6	82.98	79.33	81.21

In spite of this diversity of conditions that affect the growth and development of the beet, the differences in the percentages of water contained are not large, as the above table shows. The grand average is 82.43 per cent. The largest percentage observed was 85.64, and the smallest, 79.33. The former was from an abnormally poor beet with a sugar percentage of 7.5 while the latter was from a high-grade beet containing 14.1 per cent. sugar. With these two exceptions the range of values is from 80.24 per cent. to 84.51 per cent.

All of these figures indicate that for beets, most of which contain between 8 per cent. and 14 per cent. of sugar, 83 per cent. might be assumed as an average water factor without there being a variation in any individual case of more than 3 per cent. As has been shown above, this variation will not produce an error of more than 0.1 in the polariscope reading. In a more favorable season, or portion of a season, when the beets average better, the average water content would be lower. For use in analysis of beets which have from 12 per cent. to 16 per cent. of sugar, the factor 82 per cent. or 81.5 per cent. would probably be found to be more nearly correct. In case unusually good beets are to be analyzed, for example, beets that have previously been carefully sorted out for use as mother beets for seed production, a still lower factor—80 per cent. or 78 per cent., depending upon the richness of the beets—would be selected.

From the above discussion it will be seen that the addition to the pulp of 3.6 times its weight of water and lead subacetate solution suggested by Walawski is erroneous and would give rise to grave inaccuracies. For example, 3.6 times the normal weight (26.048) equals 93.8. 100 cc. minus 93.8 cc. equals 6.4 cc., the water presumed to be present in the beet pulp. Since 6.4 cc. or grams of water is only 25 per cent. of the weight of the sample taken, the error in the supposition is apparent.

In the same way Kaiser's proposition to add 76 cc. of water and lead subacetate solution to the normal weight of pulp would yield erroneous results, since in this case it is supposed that 24 cc. (or approximately 92 per cent. of water) is present in the beet pulp, an unknown condition. Lewenberg's modification, increasing the volume of water and lead subacetate to be added to 76.8 cc., supposes the presence of 23.2 cc., or 89.2 per cent. of water in the beet pulp. This percentage of water is still much higher than that obtained by direct determination, and would introduce a corresponding error.

Dr. Sachs' method requires the addition of 77 cc. of water and lead subacetate solution to the normal weight. In this case allowance is made for 23 cc., or 88.3 per cent. of water, in the beet pulp. This high water factor may be the source of the unsatisfactory results which he first obtained and which he attributed to incomplete diffusion of the sugar present. The experience and observation of many analysts show that the diffusion of sugar is perfect and practically instantaneous, if the pulp is sufficiently fine, when only the ordinary or normal dilution is made. This makes unnecessary the double dilution of the solution (with its attendant increase of error in the polariscopic reading) as proposed by Dr. Sachs. The error due to the incorrect value for the water coefficient would of course be diminished one-half by the double dilution, and this possibly explains the more satisfactory results that were obtained thereby.

THE PROPOSED METHOD. DETAILS OF MANIPULATION.

This being a method depending upon cold aqueous diffusion of the sugar in the beet, it is absolutely essential that the sample to be analyzed, be reduced to an impalpable pulp in order that the diffusion of the sugar throughout the solvent may be complete. The boring rasp devised by Messrs. Kiel & Dollé has been found to be well adapted for this purpose.

The sample of pulp, after being rasped to a sufficient degree of fineness, is received directly into a tared capsule of the form suggested by Le Docte[1] and the weight of the pulp ascertained. For this purpose a balance which is sensitive to one centigram is sufficiently accurate, since it is not necessary to know the weight with more exactness than the nearest centigram. The process

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[1] Spencer's "Handbook for Chemists of Beet-Sugar Houses", page 151.

of weighing may be facilitated by the use of a gram rider on the beam of the balance, in place of the usual fractional weights.

As soon as the weight of the pulp is ascertained, the volume of water to be added to this weight is read off from the table previously prepared as indicated above. Since the solution must be clarified as well as made up to definite volume, the water to be added should contain sufficient lead subacetate to clarify the mixture. For this purpose, water containing 3 per cent. by volume of a solution of lead subacetate of 54.3° Brix, or specific gravity 1.257, has been recommended and has been found to give excellent results. If it be desired to use acetic acid as recommended by Pellet, this may also be added to the water. For rapid work, the solution thus prepared should be contained in a reservoir connected with a burette having a two-way connection, which will automatically fill to the zero mark. The capsule containing the pulp is then held under this automatic burette and the volume of liquid which was ascertained from the table is discharged into the capsule. A quarter turn of the stop-cock, or proper adjustment of the pinch-cocks, closes the discharge and connects the burette with the reservoir so that it may fill to the zero, ready for the next sample.

The capsule containing the pulp thus properly diluted is then covered with a light disc of wood or glass, inclosed in a sheet of rubber so that it will fit closely to the top of the capsule and make a water-tight covering. The capsule is then grasped between the thumbs and forefingers in such a way as to press the cover down closely, and shaken vigorously. The sugar is diffused uniformly throughout the solution, practically instantaneously if the sample has been properly prepared. The cover may be coated with vaseline before use, and if slipped to one side, not lifted, in removing, it is in readiness for another determination.

The mixture is then poured on a dry filter and the remainder of the operation carried out as usual. The use of the Pellet continuous-flow observation tube materially shortens the time required for the polariscopic reading.

EXPERIMENTAL WORK.

The method thus described was used in the analysis of some sixty beets in this laboratory last fall. In every case a large sample of pulp from each beet was obtained, thoroughly

mixed to insure uniformity of composition, and then divided, one portion being analyzed by the new method and the other by the Pellet hot aqueous diffusion method—using double the normal weight of pulp and making the volume up to 202.6 cc. The beets were selected from the five different fields mentioned above, and the results obtained show that they varied in composition through wide limits. The water factor assumed in preparing the table for the analyses was 82 per cent. The beets did not prove to be so rich in sugar content as was expected, however, and the factor 83 per cent. would probably have represented more closely the average water content of the beets analyzed. This latter figure would probably have reduced somewhat the error in the results obtained for the very low-grade beets. The results of the analyses are shown in the following table:

TABLE III.—COMPARATIVE RESULTS OBTAINED BY THE NEW METHOD.

No.	Pulp taken. Grams.	Water added. cc.	Sugar by new method. Per cent.	Sugar by hot diffusion. Per cent.	Extent. of error.
1	17.33	52.34	6.2	6.25	— 0.05
2	7.61	22.95	13.6	13.7	— 0.1
3	23.34	70.50	11.9	11.9	..
4	11.88	35.88	13.1	13.05	+ 0.05
5	16.79	50.70	11.45	11.3	+ 0.15
6	12.27	37.06	11.85	11.85	..
7	25.08	75.74	5.5	5.9	— 0.4
8	18.60	56.17	10.1	10.2	— 0.1
9	23.37	70.57	10.8	10.7	+ 0.1
10	19.79	59.75	8.9	8.9	..
11	13.54	40.89	12.55	12.55	..
12	25.07	75.70	11.4	11.45	— 0.05
13	13.96	42.20	14.05	14.05	..
14	16.30	49.23	12.2	12.3	— 0.1
15	9.94	30.85	11.45	11.5	..
16	23.70	71.57	12.2	12.15	+ 0.05
17	22.79	68.80	10.0	9.95	+ 0.05
18	11.98	36.18	8.4	8.7	— 0.3
19	12.55	37.89	7.9	7.9	..
20	18.25	55.10	8.55	8.7	— 0.15
21	24.89	75.14	12.35	12.4	— 0.05
22	24.82	74.96	11.45	11.4	+ 0.05
23	17.78	53.68	10.0	9.95	+ 0.05
24	14.13	42.67	12.5	12.6	— 0.1
25	13.12	39.62	6.5	6.7	— 0.2
26	17.59	53.12	11.0	10.9	+ 0.1

No.	Pulp taken. Grams.	Water added. cc.	Sugar by new method. Per cent.	Sugar by hot diffusion. Per cent.	Extent of error.
27	21.85	66.00	10.0	9.9	+ 0.1
28	19.80	59.80	11.1	11.1	..
29	24.12	72.84	11.4	11.4	..
30	17.02	51.04	12.0	12.1	— 0.1
31	11.11	33.58	11.1	11.2	— 0.1
32	23.71	71.57	13.5	13.5	..
33	23.73	71.72	12.5	12.6	— 0.1
34	23.26	70.55	12.5	12.5	..
35	23.33	70.46	9.35	9.4	— 0.05
36	24.02	72.54	10.8	10.8	..
37	22.23	67.15	9.35	9.5	— 0.15
38	24.56	74.17	6.9	7.2	— 0.3
39	16.91	51.07	11.9	11.9	..
40	15.78	47.65	10.55	10.5	— 0.05
41	16.90	51.04	10.0	9.85	+ 0.15
42	18.32	55.33	12.45	12.55	— 0.1
43	26.04	78.64 ·	10.5	10.5	..
44	20.00	60.40	10.4	10.45	— 0.05
45	13.96	42.16	11.6	11.6	..
46	16.18	48.86	11.85	11.9	— 0.05
47	17.07	51.56	10.95	11.1	— 0.15
48	15.21	45.93	7.1	7.05	+ 0.05
49	16.19	48.90	10.8	10.9	— 0.1
50	25.28	76.35	12.95	13.0	— 0.05
51	19.96	60.28	10.4	10.35	+ 0.05
52	20.00	60.40	11.0	11.0	..
53	13.56	40.95	9.9	9.8	+ 0.1
54	14.72	44.45	8.6	8.6	..
55	13.92	42.04	11.5	11.4	+ 0.1
56	18.52	55.93	8.0	8.2	— 0.2

Of these results only five (Nos. 7, 18, 20, 27, and 56) show a variation from those obtained by the hot aqueous diffusion, greater than might be obtained from duplicate samples analyzed by the same method. The five beets which gave results too low by 0.2 per cent., or more, are all very low-grade beets from which low results might be expected owing to the increased dilution of the solution to be polarized, because of the unusual amount of water present in the beets. It is generally admitted that the hot aqueous diffusion method of analysis gives scientifically accurate results if properly carried out. Since the new method gives results which compare so favorably with those obtained by this process, its accuracy and the fact that it is based on correct principles are established.

APPLICATION OF THE METHOD TO THE ANALYSIS OF MOTHER BEETS.

The principles of the method as outlined above permit the use of certain modified forms of the apparatus employed which will decrease to a very considerable extent the time required for making a single analysis and hence increase the number of analyses which may be made in a day. The most important of these modifications are described below.

Balance—For very rapid work, an automatic and self-register-ing balance, to be used in determining the weight of the sample of pulp, is very desirable. The new form of balance recently put upon the market by Kaehler and Martini would serve very well for this purpose, since the weight of any substance placed upon the pan of the balance is indicated on the dial face directly with-out the use of weights. With such a balance, all the weighings necessary for 1,200 or 1,500 analyses per day could probably be made by two assistants, one to wipe the capsules and place them on the balance pan, and the other to read and record the weights on the slips accompanying the samples. In the absence of such a balance an ordinary chemical balance of the heavier forms, sensitive to one centigram may be used. The use of a one-gram rider on the beam in the place of the ordinary fractional weights will facilitate the weighing.

Capsules.—When large numbers of samples are to be analyzed in a very short time, the capsules into which the sample is received must all be of the same weight or tare. This can be attained by using metal capsules with a small button of tin or solder attached to the side or bottom. By filing or scratching this soft button, the weight of the capsule can be changed at will, and an equal tare for the entire set be obtained. Aluminum is a very desirable metal to be used for the construction of these capsules, since it affords the necessary rigidity and at the same time the very desirable feature of light weight. Capsules of this material are practically indestructible and are subject to only very slight changes in weight. They should be so constructed as to have a capacity of about 100 cc., and should weigh 25 to 30 grams. A shape similar to that of the ordinary porcelain cruci-ble has been found to be a very satisfactory one for these cap-sules. They may, however, be made with straight walls and a

flat bottom with rounded corners.[1] The edge, upon which the cover is to be placed in agitating the contents, should be ground flat and may be reinforced by a ring of thicker metal if sufficient rigidity cannot be obtained otherwise. An equal number of lids which will fit the capsules fairly closely should be provided, in order that the pulp may be protected from evaporation during the time which elapses between the boring of the beet and the weighing of the sample. The lid should be removed at the instant the capsule is set on the balance pan, so that the pre-arranged tare may not be disturbed. When 1,000 to 1,500 analyses per day are to be made, at least 100 of these capsules should be provided.

Burette.—A 100 cc. burette, preferably one graduated in tenths of cubic centimeters, should be used. One graduated in fifths may be employed, but more care in reading is then necessary. The burette should be provided• with an overflow at the zero mark[2] so that it will fill automatically to that point when con-nected with the reservoir containing the solution to be added. The manner of using the burette has been indicated in describing the details of the method. When used in this way, any desired volume of liquid can be quickly and accurately discharged.

The other apparatus necessary is identical with that required by any other method of analysis. A complete list of such apparatus has been published in Bulletin No. 60 of the Nebraska Experiment Station. The details of the method of obtaining the sample and of labeling the beet have been thoroughly discussed in the same bulle-tin.

THE ANALYTICAL OPERATION.

The details of the analytical operations may best be under-stood by reference to the following figure, which represents a laboratory table equipped for this work. This table should be about 14 feet in length and 3 feet in width. This size of table will permit independent action on the part of the opera-tors, and at the same time avoid the necessity of any movement from one place to another.

The capsules containing the samples of pulp are brought from the drill and placed on a table at A. The first assistant, stationed at B, takes one of the capsules, wipes off the outside, removes the

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[1] See design in Spencer's " Hand-book for Chemists of Beet-Sugar Houses", p. 181.

[2] A burette similar to that offered by Kaehler and Martini (Catalogue No. 2170) has proved to be satisfactory for this purpose.

lid, and places the capsule on the pan of the balance. The weigher C notes the weight indicated by the balance. From the reference table at his right, he ascertains the volume of water to be added to this weight of pulp and records this on the slip accompanying the sample. He then passes the capsule and its slip on to his right. In the meantime, B has prepared another
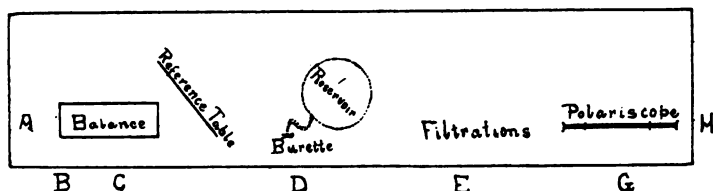
capsule and placed it on the balance pan. The operator at D then takes the weighed capsule, reads from the slip accompanying it the volume to be added, places the capsule under the automatic burette, and adds this volume of liquid. The same turn of the stop-cock which closes the discharge connects the burette with the reservoir and it is immediately filled, ready for the next sample. The capsule is at once passed on to the assistant at E, who covers it with the rubber cap, agitates it vigorously for a few seconds, and then pours the contents on a filter, which has been placed in a stemless funnel in proper position in a sugar beaker by the wash-boy stationed at J. The empty capsule is then passed across the table to the wash-boy at K, who cleans it, ready to be returned to the drill for another sample. After the filtration is complete, the assistent at G pours the filtrate into the funnel of the observation tube of the polariscope, places the accompanying slip before the observer, and passes the funnel and beaker across the table to the wash-boy at J. The latter cleans and dries them and prepares them for repeated use. The observer adjusts the polariscope, and while he is reading the scale and

recording the result on the slip before him, a new solution is poured into the observation tube by the assistant at G.

The process is thus continuous and is susceptible of great speed of manipulation. In case the ordinary form of balance is used instead of the automatic balance, a larger number of balances and assistants to operate them is, of course, necessary. By making the table wider, another row of operators might be stationed on the opposite side, thus doubling the working capacity without greatly increasing the laboratory space necessary. Care should be exercised that sufficient space for the sinks and for the wash-boys is always provided, however, since the proper cleansing and drying of the apparatus is of extreme importance.

APPLICATION OF THE NEW METHOD TO INDIRECT OR JUICE ANALYSES.

Despite the statement quoted above, that the indirect method of analysis is regarded as having "only an historic interest" it is still in very general use in this country as a means of determining the value, or purchase price, of sugar beets as they are delivered at the factories. It affords a convenient as well as fairly rapid and fairly accurate method of determining the average sugar content and purity coefficient of a composite sample consisting of quite a large number of beets of varying composition.

Several methods of obtaining a definite weight or definite volume of juice for analysis are in general use. In each of them the tendency of the somewhat viscous juice to retain bubbles of air, bits of pulp, etc., introduces more or less of inconvenience or error. The most accurate method for obtaining the desired weight of juice is by direct weighing, the so-called "gravimetric method" The same objections which were mentioned in connection with the discussion of the process of obtaining a definite weight of beet pulp are equally applicable to this procedure. It was deemed desirable, therefore, to test the accuracy of the new method when applied to the analysis of the juice of the beet.

For the purpose of calculating the volume of water and lead subacetate solution to be added, a water factor of 85 per cent. was adopted. Eight beets of different physical appearance were selected, and the juice from each obtained in the usual manner. The juice was thoroughly mixed to insure uniformity ; one sample of 26.048 grams was weighed out and analyzed by the

"gravimetric method," a second sample was measured in a sucrose pipette and the analysis completed as usual, and a third sample was analyzed by the new method. The results obtained are shown in the following table :

TABLE IV.—COMPARISON OF METHODS OF INDIRECT ANALYSIS.

Juice taken. Grams.	Liquid added. cc.	Sugar by new method. Per cent.	Sugar by gravi- metric method. Per cent.	Sugar by pipette method. Per cent.
21.78	65.12	9.75	9.8	9.8
29.92	89.46	12.8	12.8	12.65
22.04	65 97[1]	6.35	6.4	6.3
20.02	59.84	10.9	10.9	..
28.36	84.50	9.35	9.35	9.35
23.91	71.49	10.95	11.0	10.95
25.00	74.75	11.10	11.15	11.05
25.13	75.14	13.55	13.65	13.60

These few results are sufficient to show that the new method is applicable to indirect analysis. In point of accuracy it does not possess any great advantage over the sucrose pipette method if the latter is carefully carried out. It has the advantage that no specially constructed apparatus is necessary and it requires slightly less time for its manipulation than do any of the other methods.

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THE RATE OF NITRIFICATION OF SOME FERTILIZERS.

BY W. A. WITHERS AND G. S. FRAPS.

THE value of any fertilizer depends on its availability to the plant, that is, the readiness with which it can be absorbed directly by the plant, or converted into forms which can be assimilated. Nitrogen can be assimilated by plants directly in four forms; viz:—(1) free nitrogen; (2) as certain organic compounds ; (3) as ammonium salts ; (4) as nitrates.

Free nitrogen can be assimilated from the air by a class of plants with the aid of organisms living in nodules on their roots. This method of assimilation is confined to the leguminosae, which includes clover, peas, beans, the peanut, vetch, etc.

[1] Used water factor 90 per cent. in calculation.

Some organic compounds, such as urea, glycocoll, leucin, tyrosin, asparagin and acetamide, may be taken up directly by plants, and serve to nourish them. All of these compounds may occur in the soil. Urea is found in urine, asparagin in plants, and asparagin and tyrosin are often produced by the decay of animal or vegetable matter in the soil. All nitrogenous organic compounds applied to the soil change to nitrates with greater or less rapidity, and in this form are readily taken up by the plant.

Ammonium salts also can be assimilated by plants. German millet, golden millet, watermelons, corn, common sorrel, and other plants, seem to be able to assimilate ammonium salts directly. Ammonium salts also are converted to nitrates when placed in the soil.

While some plants can assimilate free nitrogen, others organic compounds, and still others nitrogen in the form of ammonia, nitrates appear to be the form in which nitrogen is taken up with the greatest readiness by most plants. It is also the form which all nitrogen compounds finally assume when placed in the soil.

When combined nitrogen, in whatever form of combination, is placed in the soil, it is converted into ammonium salts, nitrites, and finally nitrates, with greater or less speed, depending on the form of combination, the temperature, condition of the soil, etc., provided certain living organisms are present (and they usually are). If in any given soil, we determine the relative rate with which nitrogenous fertilizers which cannot be utilized directly by the plant, are converted into nitrates, it should throw some light upon the relative values to plants of those particular fertilizers.

This is the object of the work which will be described in the following pages.

HISTORICAL.

Müntz and Girard[1] have determined the relative rate of nitrification of some fertilizers. A small quantity of the fertilizer was intimately mixed with natural soil, and kept at the temperature of 15°–25° C., properly moistened, and at the end of a given period leached with water, and the nitrate determined in the extract. The nitrate existing in the soil at the beginning of the experiment was previously determined. The time was 30, 32, and 39 days for different sets. The nitrogen converted into nitrates, and the nitrogen recovered from the soil by horse-tooth corn in two years, is shown in the following table:

[1] *Central-Blatt agr. Chem.*, **20**, 656 (1891) abs.

	Nitrified in 30 days. Per cent.	Recovered by corn. Per cent.
Ammonium sulphate	75.0	76.7
Dried blood	72.4	55.0
Roasted horn, fine	71.0	60.1
Flesh meal	70.4	....
Horn trimmings, fine	55.5	53.3
Poudrette, rather coarse	18.1	14.9
Roasted leather, fine	11.6	38.3
Leather chips, raw	0.4	....

In another series, the order of nitrification was as follows: Bat guano, dried grasshoppers, dried cockchafers, flesh meal, dried blood (the substance nitrified to the greatest extent being given first). There is very little difference between the three substances named last. The nature of the soil has a great influence on the change. Nitrification was most active in a light soil from Joinville (used in the experiment referred to above), then in a garden soil, then in a chalky soil, then in a marled moor soil. Very little nitrification occurred in a very calcareous clay, except with cow manure, and yellow lupines, which loosened their texture; and none in an acid moor soil, with the same two exceptions.

P. Bonâme[1] determined the nitrates in the drainage water from a sandy soil deficient in lime to which fertilizers had been added. The order of nitrification at the end of the first month was found to be,—fish guano (most rapid), blood, fertilizer, oil cake, and ammonium sulphate. When calcium carbonate was added, nitrification took place more rapidly, but the order was still dried blood, oil cake, ammonium sulphate (see Table I).

TABLE I.

Nitrate nitrogen in 100 grams soil (in mg.)

	One month.	Two months.	Three months.
Soil	4.2	5.0	5.0
Soil and ammonium sulphate	22	29	35
Soil and dried blood	66	74	85
Soil and oil cake	59	82	95
Soil and fish guano	74	110	113
Soil and calcium carbonate	6.2	7.3	6.0
Soil, calcium carbonate, and ammonium sulphate	75	133	186
Soil, calcium carbonate, and dried blood	123	151	159
Soil, calcium carbonate, and oil cake	97	139	137

[1] *Expt. Sta. Record*, **9**, 732 abs.

It will be noted that where calcium carbonate was not used, nitrates were formed more slowly through the entire period from ammonium sulphate than from the organic substances used. When calcium carbonate was added, the quantity of nitrates produced for the first and second months from ammonium sulphate was smaller than from the organic substances.   At the end of the third month, a larger quantity of nitrates was formed from ammonium sulphate than from organic materials.

EXPERIMENTAL.

Effect of Dilution of Soil.—The effect of ratio of soil to fertilizer was studied in some preliminary experiments.   3000 grams of a sandy soil from a pasture, which had been sifted through a 6-mesh sieve, was mixed well with the quantity of dried blood containing 1.0, 0.5, 0.25, gram nitrogen, and the mixtures placed in a dark closet for fourteen days.   They were watered at suitable intervals, endeavoring to maintain the original 10 per cent. of water.   The temperature was about 27° C.   The nitrates were leached out at the end of the period, and their quantity determined by the Tiemann–Schulze method.   Results are given in Table II.

TABLE II.

	Dilution.	Nitrates. Gram.	Nitrified Per cent
Soil................................	....	0.0963	....
Soil and 1.0 gram nitrogen...........	$^1/_{3000}$	0.4564	36.0
Soil and 0.5 gram nitrogen...........	$^1/_{6000}$	0.3626	52.3
Soil, 0.5 gram nitrogen, and 1.785 gram calcium carbonate............	....	0.5043	81.6
Soil and 0.25 gram nitrogen..........	$^1/_{12000}$	0.2354	55.6

The rapidity of the nitrification is influenced very decidedly by the dilution, and increased by calcium carbonate from 100 to 156. Thirty pounds of nitrogen per acre is a liberal application for a fertilizer.   Assuming that the mean weight of a cubic foot of soil is 80 pounds, and that the soil is cultivated to the depth of 6 inches, then the dilution of the nitrogen applied as a fertilizer is $^1/_{57000}$, which is much greater than in any of the above cases.   But it must be remembered that a fertilizer is never mixed intimately with the soil, and is often in lumps, so that the actual soil surface in contact with the fertilizer is probably much less than $^1/_{12000}$. This would be particularly true with materials like dried blood, which are insoluble in water.   Soluble fertilizers, like ammonium

sulphate, would diffuse until they become fixed, or the soil water becomes of a uniform composition; the diffusion of salts in a soil must be a very slow process.

RATE OF NITRIFICATION.

The experiments to determine the relative rate of nitrification were carried out as follows: The fertilizing materials were those sent out by the referee of the Association of Official Agricultural Chemists for 1900, to test the methods for determining the availability of nitrogen. A sandy clay soil from a pasture was sifted through a coarse sieve (6 meshes to the inch), and a quantity of material equivalent to 0.6 gram nitrogen was intimately mixed with 1000 grams of the soil. The soil was then placed in precipitating jars, and kept in a dark closet, enough water being added to raise the percentage from 6.3 to 11.6 per cent. At suitable periods, three of the jars were weighed, and the estimated loss of water was replaced in all the jars. The temperature was 28°–30° C., and the time was three weeks. When calcium carbonate was added, the amount was exactly sufficient to combine with the nitrogen of the fertilizer if the entire amount were converted to nitric acid. At the end of the experiment, the nitrates were leached out, and the amount determined by the Tiemann-Schulze method. The amount of nitrates found in a blank experiment was deducted from the total. The results are given in table III.

On account of the surprisingly small percentage of ammonium sulphate nitrified in the first series, the experiments with cottonseed meal and ammonium sulphate were repeated, the time being twenty-six days, the temperature 23°–26° C., and the sample moistened as before. The soil was taken from the same pasture as in the first series, but differed from it somewhat, as is shown by the fact that it contained 0.1641 gram nitrogen as nitric acid per kilogram, whereas the former contained only 0.0595 gram.

RATE OF NITRIFICATION AND AVAILABILITY OF NITROGEN.

We have selected, and give below (Table III), the results obtained by vegetation tests with oats and Hungarian grass by Jenkins and Britton[1] and those obtained by Bizzell in the laboratory of this Station with the pepsin-hydrochloric acid method,

[1] *Conn. State Station Report* 1897, 357.

and the neutral permanganate method, the materials being those used in these nitrification experiments.

<div align="center">TABLE III.</div>

	Rate of nitrification				Availability.		
	Without		With CaCO₃.		Soluble		Vegetable
Series I.	Per cent.	Rank.	Per cent.	Rank.	KMnO₄.	Pepsin.	Test.
Dried blood........	34.8	100	54.9	100	94.4	94.7	73.3
Cottonseed meal...	33.9	97	54.8	100	91.1	91.1	64.8
Dried fish..........	30.3	87	46.5	85	88.7	67.3	63.9
Tankage...........	26.2	75	34.8	63	88.3	56.4	49.4
Bat guano..........	22.4	64	35.8	65	75.1	56.4	..
Bone	18.9	54	16.6	30	64.2	92.3	16.7
Bone (six weeks)...	21.7	..	17.4	..	..	..	..
Ammonium sulphate	1.3	4	31.1	55	100	100	..
Sodium nitrate.....	..	..	..	..	100	100	100
Series II.							
Cottonseed meal...	26.7	..	..	..	..	..	..
Ammonium sulphate	3.4	..	32.6	..	.	..	..

The order of availability as determined by the neutral permanganate method, and by the vegetation experiments, is the order of nitrification, except in the case of ammonium sulphate. The pepsin-hydrochloric acid method places bone next to blood, and above cottonseed meal, where it does not belong.

The mechanical condition of the material would, of course, have great effect on the rate of nitrification. It is quite possible that the organic fertilizers contain two or more nitrogen compounds of different degrees of susceptibility to the nitrifying organisms. Bone was nitrified to the extent of 18.9 per cent. in three weeks, and only 21.7 per cent. in six weeks.

<div align="center">EFFECT OF CALCIUM CARBONATE.</div>

Taking the quantity of nitrates formed without the presence of calcium carbonate as 100, the quantity formed with it present was, with dried blood, 158; cottonseed meal, 162; dried fish, 153; tankage, 133; bat guano, 160; bone (three weeks), 88; bone (six weeks), 80; ammonium sulphate, 2390; ammonium sulphate (Series II), 959. This effect may depend on the quantity of bases present in the material. The rate of nitrification of bone, which contains large quantities of calcium salts, is actually decreased by the addition of calcium carbonate while that of ammonium sulphate is increased enormously. These results show the bene-

ficial influence of lime in rendering nitrogenous fertilizers available, and explain in part why lime is so beneficial to many crops.

When ammonium sulphate is used as a fertilizer, it would be advisable to add calcium carbonate at the same time, in many cases.

NITRIFICATION OF AMMONIUM SULPHATE.

As regards ammonium sulphate, in a soil deficient in lime, it is nitrified less readily than any other of the fertilizing materials tested.   In the soil to which calcium carbonate had been added, the rate of its nitrification still falls below that of cottonseed meal, blood, and dried fish, and was in one series less, the other greater, than tankage and bat guano, but the average was below. In Bonâme's experiments ammonium sulphate was nitrified during the first and second months less rapidly than any of the other fertilizing materials used (blood, oil cake, guano) whether calcium carbonate was added or not.   On the contrary the experiments of Müntz and Girard (presumably in a soil containing calcium carbonate) place ammonium sulphate at the head of all the fertilizing materials tested (blood, flesh meal, poudrette, roasted leather, leather chips).

There are three possible ways to account for the slow rate of nitrification of ammonium sulphate.

1.   Ammonium sulphate may hinder the action of the nitrifying organism.   The soil in question contained 2.5 grams ammonium sulphate dissolved in 100 grams soil water.   It is known that various salts will retard the nitrifying activity of the organisms if present in too large quantity.   Deherain found that common salt began to be harmful when more than 0.1 per cent. of the weight of the soil was added, and with larger quantities nitrification almost ceased.   Large additions of sodium nitrate also decrease the rate of nitrification.

This explanation will not account for the beneficial action of calcium carbonate, for if double decomposition takes place, the ammonium carbonate formed is more of a hindrance to the germs than the ammonium sulphate.

The assumption that ammonium sulphate hinders the action of the nitrifying organism would explain the low rate of nitrification of ammonium sulphate that we have obtained.   It would also explain the results of Bonâme (already cited), according to which

ammonium sulphate is nitrified very slowly indeed the first and second months, and very rapidly the third. In direct contradiction to the above hypothesis, however, would stand the experiments of Müntz and Girard, who found that, in thirty days, ammonium sulphate was nitrified to a greater extent than dried blood, etc., and those of Th. Schloesing.[1] The latter found that at the end of fifty-six days ammonium chloride added to a soil at the rate of 3.58 grams per kilo (1.8 grams per 100 cc. of soil water) was almost completely nitrified, and the same occurred with ammonium sulphate at the rate of 2.7 grams per kilo (1.4 grams per 100 cc. soil water) in twenty-two days, and ammonium carbonate at the rate of 0.53 gram ammonia per kilo in twenty-eight days. The soil contained 19.4 per cent. water.

These difficulties might be explained by supposing that the ammonium sulphate affects the nitrifying germs less in some soils than in others, either on account of the different character of the soils (power of fixing ammonia, etc.) or the presence of different kinds of nitrifying organisms.

If the ammonium sulphate is detrimental to the nitrifying organisms, the same kind of action would take place when it is used as a fertilizer though perhaps to a less degree. Each lump of the salt would become a center from which would diffuse a solution of ammonium sulphate, detrimental to the nitrifying organisms. The time required for this unfavorable condition to disappear, would depend on the rate of diffusion of the salt, soil moisture, rainfall, etc.

2. The second explanation for the slow rate of nitrification of ammonium sulphate compared with the other materials, is that the nitric and sulphuric acids formed are detrimental to the nitrifying organisms, being only neutralized in part by the bases of the soil. When calcium carbonate is added, it neutralizes the acids, with consequent acceleration of the change. This explanation is probably applicable, but does not explain all the facts, for if so, the addition of calcium carbonate would remove the unfavorable conditions, and place ammonium sulphate at the head of the list, which it does not do.

3. The third explanation is, that different soils contain different nitrifying organisms, some of which convert organic matter directly to nitrites, while others change ammonium salts to

[1] *Central-Blatt agr. Chem.* **19**, 1 (1890) abs.

nitrites more readily.   The nitrites are then converted to nitrates.   In soils containing the first kind of organisms, and few of the second, organic matter would be converted to nitrites more rapidly than ammonium salts would be, as was the case in the experiments of Bonâme, and those here described.   In soils in which the second class of organisms predominate, ammonium salts would be nitrified more rapidly than organic compounds. This hypothesis would explain all the experiments here cited.

It appears very probable that all three of the explanations given above apply, and that all three are in operation, one exerting a greater influence in some soils than others.   It is the purpose of this Station to continue the experiments on nitrification, with a view to test all the problems that may arise.

CONCLUSIONS.

1.   The nitrification of blood takes place more rapidly when it is mixed with a large quantity of soil, than with a small quantity.

2. The order of nitrification in the soil used was, dried blood (most nitrified), dried fish, tankage, bat guano, bone, ammonium sulphate.   Excluding the ammonium sulphate, this is the order of availability, as measured by vegetation tests, and solubility in potassium permanganate.

3. When calcium carbonate was added to the soil, the nitrification was greatly accelerated, and the order became, dried blood, cottonseed meal, dried fish, bat guano, tankage, ammonium sulphate, bone.

4.   When ammonium sulphate is used as a fertilizer, in most cases it would be advisable to add calcium carbonate in some form also.

5. The low rate of nitrification of ammonium sulphate is probably due to the presence of organisms which nitrify organic compounds in preference to ammonium salts.   The presence of the ammonium sulphate may also hinder the activity of the nitrifying organisms.   The acids formed may also be a hindrance when no base is present to neutralize them.   All three of these causes may be in operation at the same time.

AN ELECTRICALLY HEATED AND ELECTRICALLY CON-
TROLLED THERMOSTAT.

BY S. W. YOUNG.

I RECENTLY found myself, on account of a very irregular and inferior gas supply, forced to devise some other means than the one usually employed, for heating and regulating the thermostat. After a few preliminary experiments the apparatus herein described was developed, and has, after considerable experience, shown itself to be thoroughly satisfactory,—in many respects more satisfactory than the usual form with gas-heating.

For this latter reason it seemed worth while to publish a brief description of the apparatus, in the hope that use might be made of it by others. As will be readily seen, the principle allows of very ready application to thermostats for biological laboratories, such as are used for the purpose of maintaining constant temperatures in paraffin baths for imbedding, etc., and for incubators and the like. Some forms of the apparatus for these purposes are being tested and, if successful, will perhaps be described elsewhere, later.

The apparatus consists of four essential parts : (1) the bath (not shown in diagram); (2) the heater; (3) the interrupter; (4) the regulator.

1. *The Bath.*—This may be of any desired form. For my purposes, I used a cylindrical agate-ware can covered with felt. The capacity was about 30 to 35 liters. The general arrangement of the bath is identical with that of the usual Ostwald thermostat and needs no further description.

2. *The Heater.*—This consists of a square board of convenient dimensions, upon which near the center are screwed two or more incandescent light receptacles, which are wired up parallel, as usual. Surrounding these is an asbestos box open at top and bottom, which serves to economize heat. For heating purposes incandescent lamps are used and have been found very satisfactory for low temperatures, although it may be questionable whether they would prove sufficiently durable at higher temperatures. For maintaining my 30-liter thermostat at 25° C., I have found that one 16 c. p. and one 8 c. p. 100 v. lamp acting

together were wholly sufficient. The four uprights at the corners of the base-board serve as supports for the bath.

3. *The Interrupter.*—This I made by the reconstruction of a telegraphic sounder. The wiring of the current to the lamps is so arranged that when the armature is raised the current passes through it and the lamps remain lighted. When the armature is pulled down the current to the lamps is interrupted at P, and the lights go out. It goes without saying that platinum contacts are preferable.

4. *The Regulator.*—This is a modification of the ordinary form of the gas regulator. The principal modification lies in the side tube S. This is provided with a piston carrying a stout iron or platinum wire W. In filling the regulator, it is so arranged that the whole space below the piston is filled with mercury and a layer of mercury is placed on the top of the piston. This allows: (1) connection between the mercury of the regulator and the battery cell; (2) it allows of the regulation of the height of the mercury in the capillary tube T, by raising and lowering the piston. In this way the regulator can be set for any desired temperature. The piston may be made of a piece of cork, fastened to the wire by cement. There is no particular difficulty in making such a piston mercury-tight. Finally the wire R is so arranged that it can be placed at any desired height in T. It serves to complete the circuit through regulator, battery, and interrupter when, by warming, the mercury shall have risen in T to such a height that contact is made with R. It also serves for the final, exact regulation of the temperature.

The action of the whole apparatus is then as follows : The bath is placed over the heater and the regulator in the bath (which must naturally be mechanically stirred); the current is turned on through the lamps which warm the bath; this warming expands the mercury and toluene in the regulator, until finally contact is made between the wire R and the mercury in T; this closes the circuit through the battery and interrupter, drawing down the armature of the latter and interrupting the current through the lamps; cooling follows, the contact between the mercury and R is broken and the current again made through the lamps. Thus the temperature in the bath is maintained constant to within small limits. In general the temperature of my thermostat never varied more than from two- to three-hundredths of a degree. By
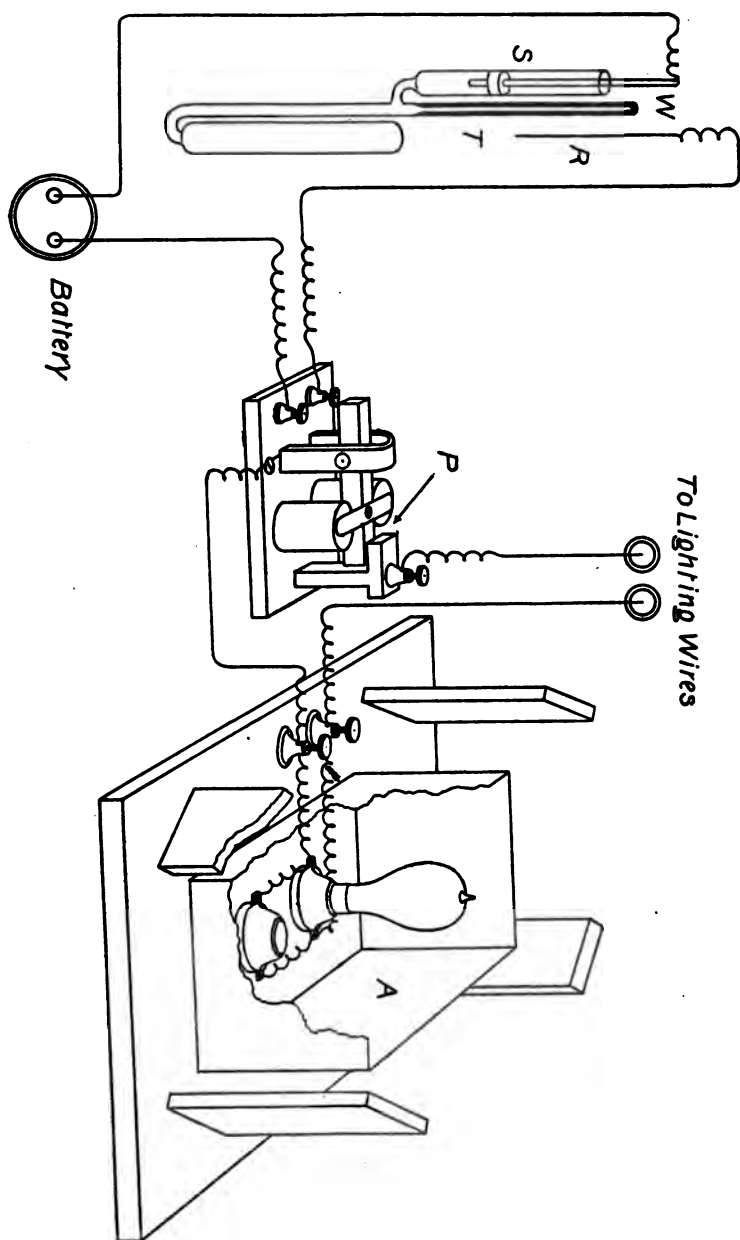
taking special precautions (avoidance of draughts, etc.), I have been able to avoid any variation greater than one-hundredth degree for over four hours. Temperature variations were noted with the aid of a Beckmann thermometer.

I should like to state here that, from my experience with thermostats, I have been convinced that the fineness of the regulation of the temperature demands not so much sensitiveness, *i. e.*, large linear motion for small temperature change in that part of the regulator where the cut-off is, but rather rapidity of response on the part of the expansive medium to temperature changes. In the ordinary bulb regulator, the lag of the expansion and contraction of the toluene is the most fruitful source of variation, when the sensitiveness of the regulator has been otherwise highly developed. This defect is to be best met, not by increasing the quantity of expansive liquid, but by distributing it in such a way that there will be greater surface exposed ; *i. e.*, in annular or spiral bulbs. I have made no experiments in this direction as the apparatus above described was wholly sufficient for my purposes.

Certain modifications of the above apparatus will naturally suggest themselves, such as use of platinum wires instead of lamps, etc., but the apparatus as described has worked so satis-factorily that I have let well enough alone.

Certain advantages, such as affording no danger from fire, cleanliness, etc., need not be enumerated here.

A METHOD FOR THE DETERMINATION OF THE AVAILABILITY OF ORGANIC NITROGEN IN COMMERCIAL FERTILIZERS.

BY JOHN PHILLIPS STREET.

OF the three essential plant-food elements, nitrogen, phosphoric acid, and potash, nitrogen is by far the most important, not only because it is the most expensive, but also because it is the chief factor from a fertilizing standpoint in the early growth of the plant. The nitrogen of sodium nitrate and that of ammonium sulphate, on account of their solubility in water, are known to be readily available to the plant, and satisfactory methods for their detection exist. The great demand for nitrogen by the farmers, however, and the desire to utilize as far as possible

all by-products have led fertilizer manufacturers to search for forms of organic nitrogen for use in the mixing of their various brands. Among those most commonly used are dried blood, dried fish, castor pomace, hoof meal, ground bone, tankage, cottonseed meal, and linseed meal. Practical experience has shown all of these forms of organic nitrogen to be quite available to the plant, and has marked them as excellent sources of plant food. The manufacturers, however, did not stop with the use of these materials, but sought still others, which were cheaper, and whose bulk was of great assistance as a filler in their fertilizers. Such materials as garbage, leather, shoddy, felt waste, and hair, came into use, and while their employment has been by no means general, it is nevertheless important to agricultural chemists that they should be able to detect these materials in mixed fertilizers, for vegetation tests have shown them to be either entirely worthless, or at any rate not available to the plant until after a comparatively long lapse of time.

The analyses made at the New Jersey Experiment Station during 1900, showed that the cost per pound of the nitrogen in different organic materials was as follows :

	Cents.
Dried blood	14.2
Dried fish	13.7
Cottonseed meal	14.5
Ground bone	16.4
Wool waste	7.0 to 0.5
Hair	5.1 to 4.6
Leather	5.0

The present laboratory methods do not determine the source of the organic nitrogen in fertilizers, and it is evident at once that the manufacturer using wool waste, hair, or leather, as the source of his nitrogen, is not justified in charging for that nitrogen the same price that he would be warranted in charging if the nitrogen of blood, fish, bone, or cottonseed meal had been utilized in making his fertilizers. To call this simply total nitrogen is manifestly unfair to the honest manufacturer, and at the same time misleads the purchaser.

At both the Connecticut and New Jersey Experiment Stations the complete fertilizers analyzed during one season were subjected to digestion with pepsin-hydrochloric acid, with the following results :

Connecticut.			New Jersey.		
Per cent. soluble.			Per cent. soluble.		
3	over	90	3	between	80 and 90
2ɛ	between	80 and 90	13	"	70 " 80
62	"	70 " 80	16	"	60 " 70
18	"	60 " 70	11	"	50 " 60
12	"	50 " 60	4	"	40 " 50
6	"	40 " 50	2 under		40
2 under		40			

A fertilizer showing 60 per cent. of its organic nitrogen soluble in pepsin may be considered as above suspicion, and one falling as low as 50 per cent. must not necessarily be condemned, while one below 50 per cent. must be regarded as suspicious. From the above table it will be seen that in Connecticut eight samples, or 6 per cent., fall in the suspicious class, and in New Jersey 6, or 12 per cent. These results show that, although their number is limited, there are suspicious fertilizers on the market, and that the necessity does exist for an accurate method to determine nitrogen availability.

For many years, therefore, agricultural chemists have employed the above-mentioned pepsin-hydrochloric acid method,[1] generally used in biochemical laboratories, as a test of the availability of organic nitrogen. Vegetation tests, and chemical tests by this method on the same materials have in general shown close agreement in most classes of organic nitrogenous compounds, but experiments at the Connecticut and New Jersey State Experiment Stations have shown that for certain classes of materials, notably hoof meal, it gives but little indication of their value. The following tabulation shows some comparative results obtained by the writer on certain well-known materials :

	Availability by	
	Vegetation tests.	Pepsin. digestion.
Dried blood	68	68
Dried fish	66	51
Hoof meal..............	62	39
Steamed bone	60	56
Tankage ....:	59	56
Wool waste.............	31	22
Raw leather	2	14

A comparison of these results shows that with the exception of raw leather, the pepsin method tends to give lower results than were secured by the vegetation tests. The pepsin results, how-

[1] Report of Conn. Expt. Station, 1893, 219.

ever, are quite satisfactory, except in the case of hoof meal, where the pepsin solubility is 23 per cent. lower than by the actual culture test.

Not only is the pepsin-hydrochloric acid method unreliable with certain materials, but it is so chronokleptic that its use is almost impossible in the average agricultural or commercial laboratory. The putrefactive method, employed in several laboratories, is open to these same objections.

While the writer was referee on nitrogen for the Association of Official Agricultural Chemists in 1895, Mr. S. H. T. Hayes, of Cornell University, submitted to him a paper in which he tested various methods for determining availability, including fractional treatment with sulphuric acid, digestion in a saturated solution of barium hydroxide, and digestion in alkaline, acid, and neutral solutions of potassium permanganate. The results obtained by Hayes[1] were not at all conclusive, but those secured by the permanganate digestion were promising, and were deemed by the writer worthy of further trial.

DIGESTION WITH POTASSIUM PERMANGANATE.

The method, as outlined by Hayes, consists in treating 1 gram of the material in a 500 cc. flask with 100 cc. of potassium permanganate solution, containing 16 grams potassium permanganate and 200 grams caustic soda per liter. Digest at a low temperature for one hour, then increase the temperature and distil for one hour, and titrate as usual. For the acid solution, the method consists in weighing 1 gram of material into a 500 cc. flask, add a little paraffin and 100 cc. of potassium permanganate solution (16 grams potassium permanganate and 100 cc. concentrated sulphuric acid to the liter). Connect with distilling apparatus, and heat at a temperature just below boiling for one hour. Then add 50 cc. of saturated caustic soda solution, distil for thirty minutes, and titrate as usual.

After making a number of tests, it was evident that the methods, as suggested, were difficult to control. It was almost impossible to carry on the digestion without a boiling of the liquid, and it was very difficult to maintain uniform conditions in two different sets of tests. Comparative results obtained by seven agricultural chemists working in different laboratories showed a wide divergence, and it was believed by the writer that this was

[1] U. S. Dept. of Agr. Dept. of Chem. Bull., 47, 112-116.

due more to this inability to control the temperature, and keep the conditions uniform, than to any inherent defect in the principle of the method itself.

It also seemed that the great variations in bulk of the nitrogenous materials examined required that the comparison should be based on the same quantity of organic nitrogen rather than on equal weights of materials. With these ideas in mind, the writer devised the following method :

Weigh an amount of the material equivalent to 0.075 gram of nitrogen into a 500 cc. Erlenmeyer flask, add 100 cc. of neutral, 1.6 per cent. potassium permanganate solution, and digest on a steam-bath for thirty minutes, shaking occasionally to moisten any particles of the material adhering to the sides of the flask. Filter and wash thoroughly, using from 125 to 150 cc. of water. Determine the total nitrogen in the undigested residue by the ordinary Kjeldahl method.

Mr. C. H. Jones,[1] of the Vermont Experiment Station, has also modified Hayes' method, by using an amount of the material equivalent to 0.045 gram of organic nitrogen with the alkaline potassium permanganate solution. The results secured by this method have on the whole been very acceptable, but with cotton-seed meal, a material of known value, it fails utterly as a test of availability.

To test the method suggested by myself, I have examined eighty-four samples of organic nitrogenous matter, representing twenty-eight different classes of fertilizing material. The results will be found in the table below, where the total organic nitrogen and the percentage digestibility in potassium permanganate are given.

AVAILABILITY OF ORGANIC NITROGEN.

	Organic nitrogen. Per cent.	Digestible. Per cent.
Dried blood	12.41	95.6
" "	13.20	95.2
" "	14.01	95.0
" "	13.60	94.4
" "	13.73	94.3
" "	14.04	94.0
" "	11.63	91.9
" "	11.39	91.8
" "	13.10	91.0

[1] U. S. Dept. of Agr., Div. of Chem., Bull. 57, 51.

	Organic nitrogen. Per cent.	Digestible. Per cent.
Dried blood	13.41	89.8
" "	11.06	87.4
Average.............	12.87	92.8
Ground horn	14.85	95.9
Concentrated tankage	11.13	93.7
Ammonite	13.00	93.6
Cracklings	13.22	93.5
Hoof meal	14.47	92.2
" "	14.04	89.7
Average.............	14.26	91.0
Castor pomace.............	6.12	90.0
Peanut pulp...............	8.52	89.3
Dried fish.................	8.78	90.2
" "	7.97	90.0
" "	7.53	88.7
" "	8.80	88.5
" "	9.53	88.0
" "	8.69	87.6
" "	7.39	87.1
" "	6.82	86.7
" "	8.28	86.5
" "	8.83	86.3
" "	9.43	86.1
" "	4.57	86.0
" "	8.37	85.0
" "	7.80	84.7
" "	6.50	82.9
" "	8.34	82.3
" "	7.75	82.2
" "	8.23	82.1
" "	5.07	81.9
" "	8.44	81.4
" "	7.49	79.6
" "	6.82	78.4
" "	5.07	74.7
" "	6.47	74.4
" "	6.86	70.1
" "	5.19	69.3
" "	6.96	65.8
Average	7.48	83.9
Tankage	6.90	91.5
"	7.67	89.5
"	5.88	87.1
"	6.42	85.4

	Organic nitrogen. Per cent.	Digestible. Per cent.
Tankage	5.69	84.0
"	6.65	81.8
"	5.67	79.8
"	5.89	79.7
"	5.34	79.7
"	5.16	65.0
Average	6.13	82.4
Cottonseed meal	7.33	79.6
" "	6.74	78.6
Average	7.04	79.1
Linseed meal	5.94	77.7
Horse meat	4.29	70.4
Steamed bone	2.78	87.0
" "	2.25	84.8
Button bone	3.33	84.0
" "	3.93	76.0
Raw bone	3.40	66.9
" "	4.12	66.3
" "	4.05	66.2
Bone sawings	3.85	77.6
Soft bone	2.37	71.6
Dissolved bone	1.95	62.7
Wool waste	2.58	77.6
" "	2.52	75.1
" "	2.51	75.0
Dissolved tankage	5.02	65.9
" "	2.93	63.1
King crab	8.78	72.5
" "	9.12	52.5
Hair manure	5.76	54.6
Garbage fertilizer	2.95	59.2
" "	3.20	44.1
Burned garbage	1.95	51.5
Steamed leather	6.87	39.5
Treated leather	7.22	33.4
Raw leather	7.56	25.5

These results are remarkably striking, the difference in the effect of the permanganate solution in the various ammoniates being very noticeable. The percentage digestibility varies from 95.9 per cent. in horn to 25.5 per cent. in raw leather. The other materials range in availability between these limits in the approximate order vegetation cultures would lead one to expect. The ground horn sample is, perhaps, somewhat above the average of

that material, it having been carefully prepared in my laboratory, and being nearly five years old and in a pulverulent condition. Of the six classes of bone examined, steamed bone shows the highest digestibility.   This is doubtless due to the fact that the process of steaming had in a large measure removed the fatty matter; raw bone, in which much fat was present, is nearly 20 per cent. lower.   The availability of the dissolved bone is slightly below that of raw bone, seeming to indicate that the treatment with sulphuric acid had little favorable effect on the nitrogenous matter in the bone ; the same conditions obtain in the case of dissolved tankage, which shows a digestibility 18 per cent. lower than the untreated tankage.   The remaining materials occupy about the rank agricultural experience would assign them.

It must be remembered in using this method, that the figures obtained are relative, not absolute.   It is not claimed that it shows the exact amount of organic nitrogen available to the plant, but it does serve as a means of distinguishing high-class from low-class ammoniates.   The results would seem to indicate that in any material showing by this method a digestibility of 60 per cent., or under, the nitrogen was obtained from an inferior source. It certainly could not have been obtained from blood, hoof meal, dried fish, tankage, or cottonseed meal, but was probably furnished by hair, garbage, leather, or some very inferior bone.

The table also shows the variations which may be found in working with materials of the same class, and indicates that the name of a fertilizer is not always a safe guide for the agriculturalist.   The variations are particularly striking in the case of fish and tankage, where the digestibility ranges from 90.2 to 69.3 and 91.5 to 65.0 per cent., respectively.   These variations are doubtless due to the varying amounts of fatty material in these products, and show still further the value of this method in the detection of such conditions.

Experiments have shown that this method is equally applicable to complete fertilizers, the only variation being that the material is washed on a filter with cold water, prior to the digestion, to remove such soluble salts as might interfere with the subsequent action of the permanganate.

It is admitted that the only true test of the availability of any fertilizer is the plant itself, but it is manifest that this method of examination is not open to all analysts, and to most is an impossi-

bility. It is hoped, therefore, that this simple method may be of value in furnishing chemists with a means of determining within reasonable limits the relative availability of the various nitrogenous materials submitted to them for examination.

LABORATORY OF THE NEW JERSEY STATE
EXPERIMENT STATION,
March 5, 1901.

AN APPARATUS FOR DETERMINING FAT.

BY H. J. WHEELER AND B. L. HARTWELL.

THE Knorr apparatus[1] for the extraction of fat, which was a great improvement over preceding forms, enabled one to dispense with the ground-glass and cork connections formerly in use, by the employment of a mercury seal.

The mercury is carried in a channel which encircles the neck of the flask at the base. In order to maintain the connection between the flask and the glass part immediately above it, the two are held together by rubber bands. To avoid the use of the bands the condensers may be made movable so they can be lowered sufficiently to connect with the flasks, or if the condensers are stationary the bath which supports the flasks may be made movable. In many instances, particularly in the case of batteries of considerable size, neither of these plans is convenient and at the best, unless great care is exercised, the flasks are liable to break during the adjustment. The use of rubber bands is unsatisfactory owing to their liability to slip or break.

A later modification of the Knorr flask was one which had a glass channel attached to the neck of the flask near the top. This modification enabled one to reduce the quantity of ether liable to collect outside of the neck, but the flask was necessarily fragile and expensive. The apparatus described below was designed to remove some of the difficulties connected with that devised by Knorr and to accomplish certain other desirable objects. The improvements attempted may be summarized as follows :

1. The use of a simple flask which can be readily cleaned and replaced at small expense.

2. The employment of a rubber cup to carry the requisite

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[1] Bull. 28, U. S. Dept. of Agriculture, Div. of Chemistry (1890), p. 96.

amount of mercury for sealing, and at the same time bind the flask firmly to the other parts of the apparatus.

3. The reduction to a minimum of the amount of ether, which can collect around the outside of the neck of the flask, by the ready adjustment of the cup to any point upon the neck.

4. The bending of the end of the tube from which the liquid ether drops upon the substance which is undergoing extraction, so that the ether will be delivered from the center and not flow down the glass.

5. The prolongation of the tube mentioned in (4) so that it may support the upper ends of extraction tubes or thimbles of different lengths.

6. The collection of the ether in one receptacle at the end of the extraction without disconnecting the apparatus.

7. The maintenance of the ether in a dry condition.

8. The loss of the least possible amount of ether vapor during the extraction and at its close.

Below is given a description of an apparatus designed to meet the conditions just mentioned. This apparatus, made in accordance with our specifications by Richards & Co., of New York, has already been in successful operation at considerable intervals for more than a year without apparent depreciation in the quality of the rubber cups and without the breakage of an extractor or other expensive glass parts.

A. A plain flask of 50 to 60 cc. capacity, having a straight neck.

B. A rubber cup channeled to carry mercury for sealing the connection between the flask and the lower portion F of the extractor.

C. A channel for mercury, showing the latter forced upward by the glass so as to cover the rubber, at the same time sealing the connection between the neck of the flask and the glass extractor which passes into the rubber cup at the outer margin of the channel.
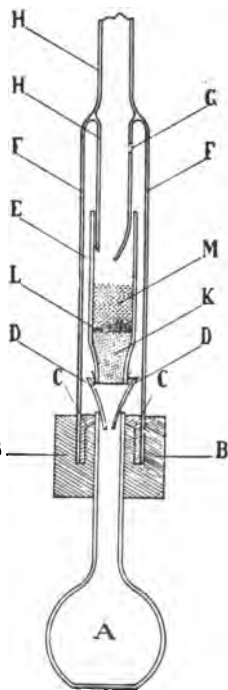
Fig. 1.

D. A small funnel to conduct the ether and dissolved fat into the flask. This is grooved where it enters the neck of the flask so that the small amount of ether which accumulates between the neck and the extractor may flow downward.

Resting upon the funnel D is the thimble which contains the material K to be extracted. The bottom of this thimble is covered with fat-free filter-paper fastened to the outside of the thimble by means of wire. The ends of the wire rest upon the edge of the funnel so as to leave space for the passage upward of ether vapor.

L. Fat-free cotton to facilitate the distribution of the ether at the beginning of or during the extraction.

M. Ether, which is maintained above the substance K in considerable quantity during most of the period of extraction. This is accomplished by raising the temperature of the flask A so that the ether may evaporate as rapidly as it filters into the flask.

E. The glass extraction tube or thimble.

F. Walls of the lower portion of the extractor.

H. The lower end of the condensing portion of the extractor, perforated at G to permit ether vapor to pass upward, and bent at an angle at the bottom so that the drops of liquid ether are delivered at the center. This part serves as a support for the thimble and is made sufficiently long to permit of the use of thimbles of various lengths.

The upper condensing portion of the extractor is of straight thin-walled glass and sufficiently long to insure condensation of the ether vapor.

The apparatus may be used singly or in battery form. The outer tubes of the condensers may be of glass, but if hot water is used in them, as described later, they should be made of metal. They are connected with the inner ones by means of rubber stoppers.

The rubber cup B binds the flask firmly to the extractor, so that rubber bands or devices for lowering or raising the bath below or the condensers above for maintaining the connection with the flask, as in the Knorr apparatus, are rendered unnecessary.

The cup also carries continually in its channel a proper amount of mercury for sealing.

In connecting and disconnecting the flask a straight cork fitting the inside of the neck of the flask A is inserted to prevent anything from falling into it as it passes through the rubber cup.
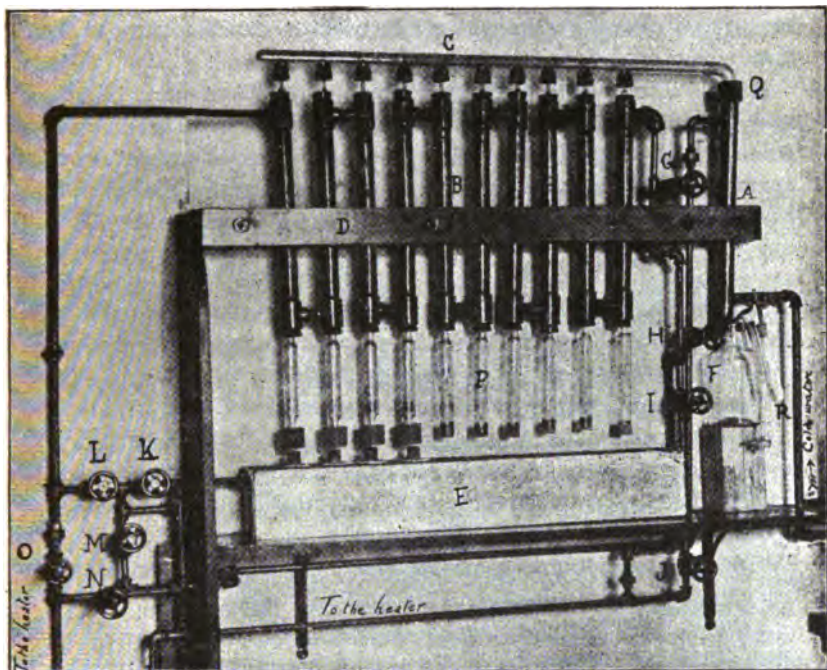
Fig. 2.

Fig. 2 shows a battery of extractors so arranged that the ether may, without disconnecting the flasks, be distilled at the close of the extraction and collected practically free from moisture. The source of heat for all the operations is an instantaneous water heater located somewhat below and (to avoid danger from fire) to the left of the battery.

BATTERY WITHOUT ARRANGEMENT FOR RECOVERING ETHER.

In laboratories where many fat determinations are made, the use of extractors in battery form is desirable. If, owing to the nature of the material to be extracted, the amount of ether necessary is considered too small to render its recovery unprofitable all of the piping necessary is that required to conduct water to

and from condenser B, and to connect the instantaneous water heater with each end of the bath E. If the apparatus is used in this manner the condenser A may be omitted, and the calcium chloride tube R attached directly to the right-hand end of tube C, which in that case may be made shorter than otherwise. A rubber tube is placed on the end of the calcium chloride tube so that it may be closed by means of a pinch-cock.

After beginning the extraction the end of the calcium chloride tube is kept open until the extractors are filled with ether vapor when it is closed and need not be opened again during the entire operation. If preferred, an automatic valve opening by pressure from within may replace the rubber tube and pinch-cock.

BATTERY COMPLETE AS SHOWN IN FIG. 2.

For the recovery of the ether the condenser A is necessary and also additional piping. The detailed arrangement of the piping will be determined by the location of the heater, the waste pipes and water supply pipes in individual laboratories.

As shown in Fig. 2, cold water after passing condenser A flows to the water heater and thence into the bath E. When the bath is once filled the water is allowed to pass through the condensers B to the waste pipe located below and to the right of valve K. During the extraction a continuous circulation is maintained from the lower right-hand end of bath E to the water heater, and thence back through the left-hand end of the bath. At the close of the extraction the cold water passing through condenser A flows to the water heater, thence to the left-hand member of battery B, forcing the cold water out underneath bath E into the waste pipe. As soon as hot water appears in the last member of battery B at the right, the current is diverted into bath E to vaporize the ether and assist in driving it over through condenser A. The water-level in bath E in the meantime is controlled by valve K in the pipe leading from the bottom of the bath to the waste; this pipe may also serve to siphon the water from the bath.

The inner tube of condenser A is straight and small enough to pass inside of tube C at the point Q where the latter is turned downward to meet it. This connection is sealed by mercury just as in the case of the flask and extractor (Fig. 1).

The tips of the inner tubes projecting through the tops of the

metal condensers B are drawn down so that they can enter the downward projections on the tube C. Short pieces of heavy-walled rubber tubing are slipped over these, and over the pieces of tubing are passed bored rubber stoppers which clasp them and the outside of the downward projections of tube C. The stopper projects considerably above the tubing so as to form a cup (about the tip) which holds sufficient mercury to produce a perfect seal over the rubber and between the two glass parts.

In setting up the apparatus the extractors P may be inserted in the condensers B before the latter are clamped in position.

The flask F is connected with the inner tube of condenser A by an ordinary cork coated with plaster of Paris. The only vent to the apparatus during the extraction and distillation is through the calcium chloride tube R attached to flask F which is kept closed the entire time after the apparatus has first been charged with ether vapor. By this arrangement no odor of ether can be detected except when the flasks are being changed and for a few moments after the extraction begins. After removing a flask from the extractor another should either be attached immediately or else the lower end of the extractor closed by means of a stopper to prevent unnecessary escape of ether vapor. It is desirable to insert a second flask at once in order that oxidation of the mercury by exposure to the air may be avoided as far as possible. In case the bath E is full of water, the extraction tube may be introduced or removed from the extractor without wetting by sliding it partially into a test-tube.

RHODE ISLAND COLLEGE OF AGRI-
CULTURE AND MECHANIC ARTS.

METHOD FOR PREPARING STRICTLY TENTH-NORMAL, FIFTH-NORMAL, ETC., HYDROCHLORIC OR NITRIC ACID.

BY RICHARD K. MEADE.

IN a paper before the Lehigh Valley Section of the Society,[1] the writer described a method for preparing strictly normal, semi-normal, decinormal, etc., sulphuric acid by decomposing copper sulphate with the electric current. Since the publication of this

[1] This Journal, **23**, 12.

paper, the following method, depending primarily upon the same reaction, has been tried and found successful, for preparing one-fifth and one-tenth normal hydrochloric and nitric acid.

The method of procedure in making tenth-normal hydrochloric acid is as follows :

12.487 grams of pure crystallized copper sulphate are dissolved in 500 cc. of distilled water in a lipped beaker capable of holding about a liter. Into this solution, after cooling if necessary, is introduced a cylinder of copper foil attached to the negative wire of an electric circuit, and a platinum rod attached to the positive wire. Both the cylinder and rod should reach to the bottom of the beaker. The copper cylinder is made from copper foil. The writer used foil 0.015 inch thick and 3 inches wide. The foil is cut the required length, which will be about three times the diameter of the beaker plus $\frac{1}{2}$ inch for a lap. The foil is curled so that the ends lap. Holes are punched through the two thick-nesses of foil with a sharp nail and wire run through these so as to fasten the two ends together. The beaker is covered with a watch-glass perforated to allow the rod to enter, and a current of from one to one and a half amperes passed through the solution for from six to eight hours or all night if the decomposition is begun in the afternoon. At the expiration of this time, the watch-glass is removed and rinsed off together with the cylinder and rod into the beaker. The solution is then transferred to a liter-gradu-ated flask and any copper that may have dropped off the cylinder into the beaker is well washed by decantation, rinsing the beaker at the same time into the flask. Now weigh, accurately, exactly 12.215 grams of crystallized barium chloride into a small beaker, dissolve in water and pour into the flask. Dilute the latter to the mark, add 2.6 cc. of water and mix well. Allow the pre-cipitate to settle, siphon off the clear liquid through a dry tube, upon a dry filter and funnel, and catch the filtrate in a dry beaker or stock-bottle.

The method depends upon the decomposition of the copper sulphate solution by the electric current into copper and sulphuric acid. Upon adding barium chloride to this latter, double decom-position takes place, and barium sulphate and hydrochloric acid are formed. The addition of the 2.6 cc. of water after the solu-tion has been made up to the mark, is to correct for the volume of water displaced by the precipitate.

In preparing tenth-normal nitric acid by this method, the only change that is made is in the substitution of 13.076 grams of barium nitrate for the barium chloride. The quantity of copper sulphate, of course, remains the same.

In preparing large quantities of the acid it would probably be simpler to pour the solution into a stock-bottle, provided with a siphon, immediately after adding the barium chloride or nitrate, making up to the proper volume and mixing. The solution can then be drawn off for use as wanted, after the precipitate has settled. The siphon tube must not reach so near the bottom of the bottle as to stir up the precipitate. Graduated flasks as large as two liters are carried in stock by dealers in such ware. When it is desirable to make up larger quantities of acid, ungraduated flasks can be purchased, holding as much as 10 or 12 liters. Their exact volume to any point on the neck can be found either by weighing water into them if a sufficiently large delicate balance is at hand or even by measuring water into them; the proper amounts of copper sulphate and barium chloride or nitrate can then be calculated and used to make this volume. In calibrating the flask by measuring water into it, it must be borne in mind that the ordinary flask is graduated to hold, not to deliver, the given volume. To find the volume a given flask will deliver, weigh into it say 100 grams of water from a weighing-bottle, revolve the flask so as to wet the sides, then pour the water back and drain the flask into the weighing-bottle for one minute. The loss in weight, on again weighing the water, may be taken as the correction to be subtracted from the volume which the flask is graduated to contain for the volume it will deliver. This method will be sufficiently accurate for the present purpose.

I have prepared only tenth-normal and fifth-normal acids by this method. Probably normal acid could also be prepared though the waste, due to the solution retained in the precipitate, would, of course, be greater owing to the larger volume of the latter.

In the first attempts to prepare tenth-normal acid by this method the barium chloride was added to the solution after the cylinder and rod had been removed and before making up to the liter. The solution was then filtered into the graduated flask after the precipitate had settled, and the latter brought upon the

paper and washed with hot water until the mark on the neck of the flask was reached. The solution was then cooled and made up to the liter. The solution, on testing, however, proved to be a little below the desired strength, due no doubt to the "holding back" of some of the acid by the precipitate. The method first given was then tried and gave a solution of the exact strength desired with much less labor and in much less time.

Both the nitric and hydrochloric acid solutions were tested as follows:

Fifty cc. of the acid were made alkaline with ammonia, heated to boiling, and ammonium oxalate added. No precipitate formed in any case.

Fifty cc. were heated to boiling and barium chloride added. Only a very slight cloud formed. The precipitate was allowed to stand over night in a warm place, filtered, washed, ignited, and weighed. The results on the five solutions were as follows:

No.	Solution.	BaSO$_4$ in 50 cc. Gram.	H$_2$SO$_4$ in 50 cc. Gram.	H$_2$SO$_4$ in 1 liter. Gram.
1	0.1 N HCl	0.0004	0.00017	0.0034
2	0.1 N HCl	0.0008	0.00034	0.0068
3	0.2 N HCl	0.0030	0.00126	0.0252
4	0.1 N HNO$_3$....	0.0025	0.00105	0.0210
5	0.2 N HNO$_3$....	0.0038	0.00160	0.0320

Where the standard hydrochloric acid is intended for use in determining the alkaline earths, it would, of course, be necessary to add a little in excess of 12.215 grams of barium chloride, the theoretical quantity necessary to convert the sulphuric acid to tenth-normal hydrochloric acid. Indeed it would, perhaps, be better in all cases to add a slight excess of the salt since a trace of it in the solution can certainly, in most cases, do no harm.

When checked against nearly tenth-normal sodium hydroxide solution (which had been prepared from metallic sodium, carefully standardized, and kept free from carbon dioxide), using phenolphthalein as an indicator, the results showed each solution prepared to be of exact strength, as the following will show:

No.	Solution.	Standard acid taken for the test. cc.	Standard sodium hydroxide required. cc.	Equivalent volume of 0.10 N NaOH.[1] cc.
1	0.1 N HCl...............	10.0	10.2	10.01
		10.0	10.2	10.01
		10.0	10.2	10.01
		20.0	20.4	20.02

[1] Factor for converting standard sodium hydroxide to 0.1 N NaOH = 0.9813.

No.	Solution.	Standard acid taken for the test. cc.	Standard sodium hydroxide required. . cc.	Equivalent volume of 0.10 N NaOH. cc.
2	0.1 N HCl	10.0	10.2	10.01
		10.0	10,2	10.01
		20.0	20.4	20.02
3	0.2 N HCl	10.0	20.4	20.02
		10.0	20.35	19.97
		20.0	40.75	40.00
4	0.1 N HNO$_3$	10.0	10.2	10.01
		10.0	10.2	10.01
		20.0	20.4	20.02
5	0.2 N HNO$_3$	10.0	20.4	20.02
		10.0	20.4	20.02
		20.0	40.7	39.94
		20.0	40.75	40.00

EASTON, PA., April 1, 1901.

THE COMPOSITION OF JELLIES AND JAMS.

BY L. M. TOLMAN, L. S. MUNSON, AND W. D. BIGELOW.

A S preliminary to the examination of a large number of samples of commercial fruit preserves, it was thought desirable to have, as a basis of comparison, the analyses of fruits and fruit products of known origin, as the work with this class of foods has been largely confined to the detection of adulterations rather than to the proximate analysis. Accordingly, such whole fruits as were to be obtained were purchased, and from these the juices, jellies, and jams were prepared. The juices were prepared by cooking the cleaned fruit, with enough water to prevent scorching, till it became soft, and straining through a jelly-bag. In the preparation of the jellies, equal parts of the strained juice and cane-sugar were used and were heated to the point of boiling, which required about twenty minutes.

With the jams approximately one part of sugar was used to two parts of the crushed fruit, heated to boiling, and this temperature maintained for about twenty minutes. In all cases the original fruit and sugar, as well as the final products, were weighed which gave a basis for estimating the amount of added cane-sugar in the finished product.

It is to be regretted that the fruits selected were not in all cases of typical composition. This is especially true of the apples and grapes. This, however, will not lessen their value for studying the sugar content. In comparing the composition of jellies

and jams with that of the juices and pulps from which they were prepared, allowance must be made for the changes in composition resulting from the evaporation of water and the loss of proteid and other matter in the scum that rises in the process of preparation.

METHODS OF ANALYSIS.

With the juices and thoroughly pulped fruits and jams, weighed amounts were taken for each determination. With the jellies, it was found more convenient to dissolve 50 grams of the material in water and make it up in volume to 500 cc. Then aliquot portions were taken for solids, ash, acids, nitrogen, and reducing sugars.

Total solids were determined in about 10 grams of the juice and the crushed fruits, and about 5 grams of the jellies and jams, by drying in large flat-bottomed platinum dishes at a temperature of 100° for ten to twelve hours. The writers recognize that drying in vacuo at a low temperature is preferable, but since that would be impracticable with the large volume of work planned with commercial products, it was not done with these samples. Water in sufficient quantity to make them flow readily was mixed with the portion of the jams and crushed fruit taken for the determination of total solids, so that they could be distributed in an even layer over the bottom of the dish.

To estimate the ash the residue obtained in the determination of total solids was thoroughly charred, exhausted with water, the insoluble portion washed with water and collected on a filter. The filter-paper and contents were then returned to the dish and ignited to whiteness, the soluble ash, and a few drops of ammonium carbonate solution added, and the whole evaporated to dryness, heated to low redness, and weighed.

In the estimation of acidity about 10 grams were dissolved in hot water and diluted to about 400 cc. with recently boiled water. A few drops of phenolphthalein solution were then added and the mixture titrated with a decinormal solution of potassium hydroxide. The end point was easily observed even in highly colored fruits. Owing to the dissimilarity of the various fruits in their characteristic acids, it is found advantageous to express acidity in terms of one acid instead of the acid characteristic of the particular fruit which is supposed to be present. The use of an acid, which occurs in some fruits and not in others, is likely to lead to confusion. The writers prefer the custom which

is practiced in many laboratories of expressing results in terms of sulphuric acid (H_2SO_4).

Nitrogen was determined by the Gunning method in such an amount of material as would give about 2 grams of dry matter and the result multiplied by 6.25 for the proteid content.

Reducing sugars were determined by the regular Allihn method.[1]

Cane-sugar was calculated from the direct and invert polarizations by the Clerget formula

$$S = \frac{A - B}{144 - \frac{2}{t}}.$$

Polarizations were made upon normal weights of the juices and fruits and upon half-normal weights of the jellies and jams, with the Schmidt and Haensch instrument, using a 200 mm. tube. All results were calculated to normal weights.

As is well known the sugars of the fruits are largely reducing sugars, but in all the fruits examined, except the blackberry, cane-sugar was found in varying amounts. In the orange, peach, and pineapple it was in excess of the reducing sugar.

The polarization of the Damson plum is peculiar in that the invert reading at 86° is positive, indicating an excess of dextrose over levulose, while all the other fruits have either a zero or a negative reading at this temperature.

The inversion in the preparation of jams and jellies of the added cane-sugar is of particular interest. As might be expected the extent of inversion varies in general with the amount of free organic acid present, and with the length of the time the product is heated. Still the different fruit acids vary widely in their inverting action upon cane-sugar and consequently there are some marked exceptions to the general rule mentioned above. For example, in crab apple jelly, with 0.17 per cent. acid, 58.8 per cent. of the cane-sugar was inverted, while with the orange jelly of the same acid content only 4.9 per cent. was inverted. With the fox grape jam containing 0.69 per cent. acid, 92.9 per cent. of cane-sugar was inverted, while with wild fox plum containing 1.35 per cent. acid only 53.4 was inverted. The crab apple excepted, the jams and marmalades showed a higher per cent. of inversion than the corresponding jellies, owing to the fact that they were heated for a much longer time.

[1] Bulletin 46: Rev. U. S. Department of Agriculture, Division of Chemistry.

TABLE I.—JUICE.[1]

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H_2SO_4. Per cent.	Proteids (N × 6.25). Per cent.	Reducing sugar. Per cent.	Cane-sugar added. Per cent.	Cane-sugar found. Per cent.	Added cane-sugar inverted. Per cent.	Polarisation. Direct at at 18° C.	Invert at 18° C.	Invert at 88° C.
20400	Apple (fall pippin)	7.95	0.47	0.627	0.543	4.00	....	1.18	....	— 3.0	— 4.6	— 2.9
20396	Blackberry	8.54	0.52	0.978	0.350	4.34	....	0.00	....	— 1.5	— 1.6	— 1.0
20403	Crab apple	5.62	0.20	0.372	0.075	2.56	....	1.03	....	— 1.0	— 2.4	— 1.1
20428	Grape (fox)	6.67	0.49	1.686	....	2.79	....	0.37	....	— 0.8	— 1.3	— 1.1
20401	Grape (Ives seedling)	8.83	0.57	0.902	0.237	5.10	....	0.89	....	— 1.2	— 2.4	— 0.6
20397	Huckleberry	16.33	0.40	0.454	....	11.21	....	0.89	....	— 3.2	— 4.4	— 0.9
20430	Orange (Florida navel)	6.08	0.36	0.297	0.581	1.52	....	2.29	....	+ 1.8	— 1.3	0.0
20427	Peach	8.90	0.45	....	0.218	....	....	4.59	....	+ 4.0	— 2.2	— 0.7
20431	Pear (Bartlett)	11.65	0.45	0.345	0.087	5.87	....	1.18	....	+ 4.8	— 6.4	— 4.0
20429	Pineapple	13.27	0.45	0.588	0.368	2.74	....	8.96	....	+ 8.4	— 3.7	— 1.1
20426	Pineapple husk juice	8.43	0.77	....	0.350	....	....	4.73	....	+ 4.1	— 2.3	— 0.7
20399	Plum (Damson)	12.72	0.63	....	0.431	4.86	....	0.51	....	+ 2.0	+ 1.3	+ 2.4
20402	Plum (wild fox)	11.23	0.64	1.576	0.137	2.87	....	2.81	....	+ 1.4	— 2.4	— 1.8
20398	Mixed fruit	6.53	0.32	0.612	0.150	2.68	....	0.59	....	— 1.0	— 1.8	— 0.9

[1] The "juice" was prepared by cooking the fruit till soft, after the addition of sufficient water to prevent scorching, and straining through a jelly bag.

TABLE II.—JELLY.

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H₂SO₄. Per cent.	Proteids (N × 6.25). Per cent.	Reducing sugars. Per cent.	Cane-sugar added. Per cent.	Cane-sugar found. Per cent.	Added cane-sugar inverted. Per cent.	Direct at 18° C.	Invert at 18° C.	Invert at 87° C.
20408	Apple (fall pippin)	59.18	0.22	0.279	0.175	20.78	51.76	33.04	36.17	+ 24.0	— 20.6	— 1.2
20405	Blackberry	59.63	0.33	0.475	0.243	12.51	54.89	44.90	18.20	+ 47.0	— 20.1	0.0
20410	Crab apple	63.28	0.11	0.171	0.137	34.93	57.61	23.68	58.88	+ 13.0	— 19.0	0.0
20405	Grape (Ives seedling)	63.66	0.45	0.524	0.175	32.29	60.29	30.52	49.33	+ 22.3	— 18.9	+ 0.2
20412	Huckleberry	63.02	0.28	0.245	0.069	24.27	53.39	32.74	37.54	+ 24.1	— 20.1	— 0.4
20435	Orange (Florida navel)	68.56	0.30	0.171	0.418	3.95	65.59	62.52	4.91	+ 61.3	— 23.1	— 0.2
20437	Peach	69.98	0.21	0.245	0.175	8.75	63.70	56.59	11.16	+ 53.4	— 23.0	— 0.6
20434	Pear (Bartlett)	69.12	0.34	0.181	0.156	6.58	63.09	58.46	7.33	+ 52.7	— 26.2	— 1.8
20436	Pineapple	80.28	0.43	0.328	0.387	22.13	72.98	56.70	28.45	+ 50.4	— 26.1	0.0
20433	Pineapple husk	76.34	0.73	0.352	0.350	7.40	70.22	65.22	7.12	+ 63.7	— 24.3	— 0.6
20404	Plum (Damson)	45.56	0.68	1.127	0.350	19.18	38.00	22.67	40.38	+ 17.8	— 12.8	0.0
20409	Plum (wild fox)	54.49	0.40	1.029	0.138	24.00	48.05	25.48	46.97	+ 16.7	— 17.8	0.0
20411	Plum (wild fox) boiled down	73.01	0.65	1.529	0.175	44.22	64.66	22.37	66.18	+ 7.6	— 22.6	— 0.6
20407	Mixed fruit	66.58	0.81	0.367	0.069	39.70	59.72	24.22	40.38	+ 14.8	— 17.9	+ 2.2

TABLE III.—FRUIT.[1]

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H₂SO₄. Per cent.	Proteids (N × 6.25). Per cent.	Sugars.				Polarizations.		
						Reducing sugars. Per cent.	Cane-sugar added. Per cent.	Cane-sugar found. Per cent.	Added cane-sugar inverted. Per cent.	Direct at 18° C.	Invert at 18° C.	Invert at 86° C.
20449	Apple (fall pippin).....	8.25	0.30	0.499	....	4.13	....	1.03	....	− 2.2	− 3.6	− 1.8
20415	Blackberry.............	9.62	0.60	0.916	0.725	5.67	....	....	....	− 1.1	− 1.0	0.0
20418	Crab apple............	14.34	0.84	0.705	0.418	5.68	....	1.70	....	− 0.7	− 3.0	− 0.8
20417	Grape (Ives seedling)...	12.50	0.75	....	....	6.11	....	0.29	....	− 1.6	− 2.0	0.0
20425	Orange (Florida navel) .	13.11	0.61	0.686	0.985	4.13	....	3.33	....	+ 2.0	− 2.5	− 0.8
20444	Pineapple	13.71	0.50	0.392	0.056	8.12	....	3.11	....	+ 1.0	− 3.2	0.0

[1] The composition here given is not that of the original fruit, but of the pulped mass used in the preparation of jams.

TABLE IV.—JAM.

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H_2SO_4. Per cent.	Proteids (N × 6.25). Per cent.	Sugars.				Polarizations.		
						Reducing sugars. Per cent.	Cane-sugar added. Per cent.	Cane-sugar found. Per cent.	Added cane-sugar inverted. Per cent.	Direct at 18° C.	Invert at 18° C.	Invert at 86° C.
20446	Apple (fall pippin)........	63.22	0.20	0.282	0.175	25.52	51.31	29.11	43.22	+26.3	−13.0	+4.8
20414	Blackberry	55.42	0.48	0.851	0.737	18.77	43.99	29.00	34.08	+24.6	−14.6	+1.6
20419	Crab apple...............	41.82	0.27	0.715	0.493	14.80	36.09	23.04	35.46	+18.3	−12.8	−0.6
20445	Grape (fox)	61.80	0.19	0.698	0.200	50.06	54.21	3.70	92.96	−9.0	−14.0	+2.2
20416	Grape (Ives seedling)..	56.64	0.48	0.744	0.525	33.44	42.45	11.33	73.38	+3.5	−11.8	0.0
20443	Orange (Florida navel).	80.52	0.44	0.433	0.944	13.61	69.13	54.23	21.55	+55.9	−17.5	+2.0
20448	Pear (Bartlett)..........	61.52	0.28	0.163	0.312	13.20	46.52	33.74	18.87	+32.3	−13.2	+1.0
20442	Pineapple marmalade .	73.92	0.30	0.315	0.312	14.05	60.20	46.40	22.90	+52.3	−10.3	+6.2
20421	Plum (Damson)	50.43	0.54	1.012	0.525	28.29	37.75	9.70	74.42	+3.1	−10.0	+1.2
20423	Plum (wild fox)........	62.10	0.46	1.355	0.212	28.78	47.86	23.26	53.43	+13.9	−17.5	0.0

ON THE DETERMINATION OF HYDROGEN IN GAS MIX-
TURES.

BY FRANCIS C. PHILLIPS.

THE strongly exothermic character of the reaction involved in the combustion of hydrogen renders it possible to determine this gas by oxidation over palladium asbestos without the application of external heat. As the moisture produced in the reaction is liable to condense and cause the palladium to become wet, it is usual to apply heat in order to prevent this condensation and to insure the completeness of the reaction. For this purpose Winkler[1] recommends the use of a gas flame placed directly below the palladium asbestos tube. In heating over a flame the obvious danger occurs of burning hydrocarbons along with the hydrogen. The use of hot water as a source of heat presents the advantage that the temperature of the palladium is prevented from rising much above 100° C., provided that the rate of passage of the gas through the palladium asbestos tube is slow. Still it is somewhat difficult by any existing device to preserve a constant and definite temperature. The form of apparatus described below has proved convenient for maintaining the palladium asbestos at the temperature of boiling water for a period of time sufficient for the performance of a series of hydrogen determinations.

In the drawing, which represents the apparatus in section, *a a*
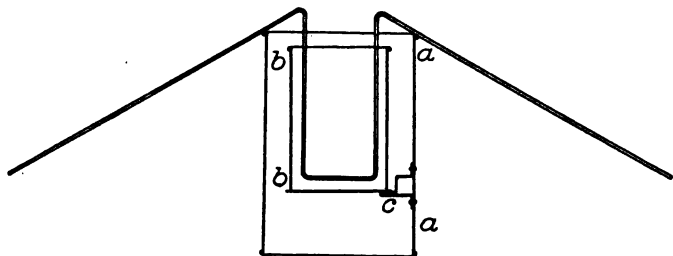
is a brass cylinder 30 cm. long and 18 cm. wide. It is open at both ends, the rims being strengthened by wires. *b b* is a cup-shaped vessel 18 cc. deep and 12 cc. wide. When in use this inner vessel rests upon three supports which are riveted to the

[1] Winkler and Lunge : "Handbuch of Technical Gas Analysis," 1885, p. 79.

inner surface of the cylinder *a a*. One of these supports is shown at *c*. The space between the cup and the cylinder is nearly 3 cm. wide. The cup is silvered on the outside and the cylinder is silvered on both sides. Any of the mixtures which are sold for giving a silver coating to brass will serve for the purpose.[1] The palladium asbestos is introduced into the middle of a glass tube 70 cm. long and about 3 mm. in internal diameter. The tube is then bent into the form shown in the sketch and the U-shaped part placed in the brass cup, which is then filled with water. A small flame is kept burning under the cup and the water maintained at a temperature approaching the boiling-point. The glass tube containing the palladium asbestos is connected at one end with a gas burette and at the other end with a Hempel pipette. The gas in which the hydrogen is to be determined, together with the necessary volume of air having been introduced into the burette, and the water-levels being carefully adjusted, the gas is caused to flow slowly through the palladium asbestos tube into the pipette, and back again to the burette, the volume of the hydrogen being ascertained in the usual manner. The polished silver surfaces prevent radiation to such an extent that the accuracy of the gas measurements is not affected by the close proximity of the measuring apparatus to the source of heat.

The palladium asbestos is prepared by moistening long-fibered asbestos with palladium chloride solution and igniting over a Bunsen burner flame, the process being repeated until the asbestos receives a sufficient quantity of the reduced metal (about 6 per cent. of the weight of the original asbestos has been found to be a convenient proportion). The deposition of the palladium occurs mainly on the surface of the bundle of asbestos fibers. It is well, therefore, in order to distribute the reduced metal as evenly as possible throughout the mass of the asbestos, to roll the fibers under a glass rod on a glass plate once or twice during the process of alternately impregnating with palladium chloride and igniting. Minute crusts of palladium accumulated upon the surface of the asbestos are liable to glow intensely, even when the

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[1] A silvering mixture may be prepared according to the following formula : Dissolve 8 grams of silver nitrate, 10 grams of potassium cyanide, and 0.5 gram of potassium tartrate in 100 cc. of water. Add sufficient French chalk to make a thin paste. This mixture, applied with friction by help of a piece of Canton flannel, will produce a highly lustrous silver surface upon brass or copper.

tube is immersed in water, during the passage of a gas containing hydrogen and oxygen, and by so doing cause a partial combustion of any hydrocarbons that may be present. It is important, therefore, that the palladium should be distributed as uniformly as possible throughout the asbestos. As a result of the ignition, after impregnation with palladium chloride solution, the asbestos becomes somewhat more rigid and the bundle of fibers may be readily pushed, by help of a copper wire, far into the narrow glass tube.

ON THE SEPARATION OF TUNGSTIC AND SILICIC ACIDS.

BY H. L. WELLS AND F. J. METZGER.

IN a recent number of a German periodical[1] appears an article by Otto Herting, of Philadelphia, in which the assertion is made that the method given in the text-books for expelling silica from tungstic acid by means of hydrofluoric acid is incorrect. This statement is made on the ground of alleged numerous quantitative experiments with mixtures of pure tungstic acid and pure ignited silicic acid, but no details in regard to the results are given. Herting believes that upon ignition, silicic and tungstic acids form a silicotungstic acid which is volatile when treated with hydrofluoric acid, and finally says that he should be pleased if, by means of his article, he should bring about the more careful study of the "action of hydrofluoric acid upon tungstic acid in the presence of silicic acid."

Since Herting's statement throws doubt upon a method that is generally used, we have undertaken an examination of the matter. For this purpose, we dissolved some of Kahlbaum's tungstic acid in ammonia, precipitated with nitric acid, washed with water by decantation, digested repeatedly with sulphuric acid of sp. gr. 1.378 to separate any molybdic acid that might possibly be present,[2] washed the residue and ignited it. The tungstic acid thus prepared was used for the experiments that follow.

A weighed quantity of tungstic acid in a platinum crucible

[1] *Ztschr. angew Chem.*, 1901, 165.
[2] See Ruegenberger and Smith : This Journal, **22**, 772.

was mixed with about an equal quantity of pure silica. The mixture was covered with dilute sulphuric acid, a liberal amount of pure hydrofluoric acid added, the liquid carefully evaporated, and the residue ignited over a Bunsen burner. Then another portion of silica was added and the operation repeated. The results are shown in the following table:

| | Taken. | | Tungsten trioxide found after | |
	Tungsten trioxide. Gram.	Silica. Gram.	First operation. Gram.	Second operation. Gram.
I.	0.1928	0.2	0.1927	0.1928
II.	0.2097	0.2	0.2097	0.2096
III.	0.2100	0.2	0.2099	0.2100
IV.	0.1999	0.2	0.2000	0.1998

The greatest error found in these experiments is 0.0001 gram and they show that the process is perfectly exact under these conditions.

Other experiments showed that long ignition of the mixed tungstic and silicic acids over the Bunsen burner before expelling the silicic acid had absolutely no effect upon the results. It was thought that in the absence of sulphuric acid a loss might occur by the treatment of tungstic acid with hydrofluoric acid, and the following experiments were made to test this point, no sulphuric acid being used:

| Taken. | | Tungsten triox- |
Tungsten trioxide. Gram.	Silica. Gram.	ide found. Gram.
0.1983	0.2	0.1983
0.2102	0.2	0.2100
0.2106	0.2	0.2105
0.1996	0.2	0.1994

In these experiments, the greatest error, 0.0002 gram, is well within reasonable limits; hence, it is evident that the absence of sulphuric acid has no effect. It is to be noticed that in these cases also, the tungstic acid was ignited by the Bunsen flame only.

Attention should be called to the fact that tungstic acid must not be ignited by means of the blast-lamp, since at the temperature thus produced, it volatilizes to a considerable extent. The books of reference do not give proper warning in regard to this matter. The following table gives the results of a series of experiments made by heating some of the substance (which showed no loss of weight over the Bunsen burner) over the blast-lamp in a platinum crucible:

	Weight of tungsten trioxide. Gram.	Loss. Gram.
Taken	0.3007	......
Ignited for two minutes.............	0.2978	0.0029
" " " " again	0.2962	0.0016
" " " " "	0.2946	0.0016
" " " " "	0.2932	0.0014
" " " " "	0.2924	0.0008
" " " " "	0.2916	0.0008
" " " " "	0.2906	0.0010
" " five " "	0.2872	0.0034

Total loss.... 0.0135

All the ignitions except the last were made with a lamp provided with a water-blast, which gave a flame of only moderate power. The last ignition was made with a lamp connected with a foot bellows, which gave a considerably higher temperature. It is noticeable that the losses show a tendency to diminish after the first ignition, but this is probably due to a change in the physical condition of the oxide rather than to the removal of some more volatile substance. It is hardly possible that our carefully purified tungstic acid, which showed no loss when heated with a good Bunsen burner, could contain an amount of molybdic acid or other volatile substance sufficient to give the results that have been obtained. The loss shown in the table above amounts to nearly 5 per cent., while in an other experiment 0.1955 gram of tungstic acid lost over 7 per cent. after heating with the blast-lamp for twenty minutes. It should be stated that the platinum crucible in which these ignitions were made showed no loss in weight after it had been cleaned.

We have shown that Herting's criticism of the usual method for separating silicic and tungstic acids is without foundation, and it appears probable that his difficulties were due to igniting tungstic acid at a too elevated temperature.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1901.

POTASSIUM PERSELENATE[1]—PRELIMINARY NOTE.

By L. M. DENNIS AND O. W. BROWN.

POTASSIUM perselenate was prepared by the electrolysis of a saturated solution of potassium selenate containing a little free selenic acid. This solution was placed in a 150 cc.

[1] The experimental work herein described was performed by Mr. Brown in the spring of 1898. It has been impossible to resume the work until recently, but it is hoped that the investigation may soon be carried to completion.

beaker and the anode, a platinum plate of about 15 sq. cm. surface, was introduced into it. The cathode, a piece of platinum foil, was contained in a small porous cup of about 75 cc. capacity which was suspended in the solution. This porous cup was filled with a dilute solution of selenic acid. The beaker was placed in a freezing-mixture and a current varying from 2.5 to 3 amperes was passed through the solution. The temperature in the outer cell averaged about 4° C.

After the action of the current had continued for some hours, a white substance began to appear in the neighborhood of the anode, its formation being accompanied by an increase in the resistance of the cell. After considerable of the solid had separated, the process was interrupted, the solution in the beaker was decanted, and the substance dried on a porous plate. It was then placed in a desiccator containing phosphorus pentoxide, and this was placed upon ice.

The complete analysis of the substance was not made at the time but merely the available oxygen was determined, this being done, first by adding oxalic acid in excess and determining the excess by means of potassium permanganate, and second, by adding ammonium ferrous sulphate in excess and titrating this excess in the same manner.

The two methods gave agreeing results, for when used on a sample of potassium selenate containing a small amount of perselenate, oxalic acid and potassium permanganate showed 2.41 per cent. of $KSeO_4$, while the ammonium ferrous sulphate method gave 2.42 per cent.

Potassium perselenate was not obtained free from selenate, the highest percentage of perselenate in the product being 74.44.

Potassium perselenate, when hot, oxidizes manganese dioxide to potassium permanganate, quickly oxidizes ferrous sulphate in the cold, and acts similarly upon thallous sulphate. An aqueous solution of the salt gives off oxygen when warmed.

CORNELL UNIVERSITY,
April, 1901.

NOTES.

On Methods of Sugar Analysis.—In the March number of the Journal of the American Chemical Society there is published a paper by Professor H. W. Wiley on "The Fourth International

Congress of Applied Chemistry,'' which, it appears, was read
before the Northeastern Section of the American Chemical
Society, January 17, 1901.

In that article (on page 188) Professor Wiley refers to some
of the topics which engaged the attention of the "International
Committee on Unification of Methods of Sugar Analysis.''

Professor Wiley writes : " In the meeting of this committee,
the data relating to the influence of temperature on polarizations
were presented at length by M. Wiley of the United States, and
M. Brodhun, of Germany. The only advocate of the stability
of specific rotation, independent of temperature, was M. Wiech-
mann of the United States. The opinions of the majority were
embodied in a resolution which finally passed the International
Committee without a dissenting vote. This resolution was to
the effect ''...(For wording of this resolution, see this Journal,
Vol. 23, page 62). Professor Wiley continues : "The influ-
ence of temperature on specific rotation has now been so
thoroughly worked out that we may say without hesitation that
the points established by Andrews eleven years ago, are now
fully accepted by practically all the investigators of the world.''

These statements tend to give to one not familiar with the
facts, the impression that the majority of the members present
indorsed the opinion, that the specific rotatory power of sucrose
is affected by changes in temperature.

As a matter of fact the International Committee studiously
avoided any expression of opinion on this question which had
been a prominent topic of discussion between Professor Wiley
and myself that day, before this body.

It was for this very reason that Professor Wiley's resolution,
that his method of correcting polarization readings for the influ-
ence of temperature be adopted, was not accepted by the com-
mittee. Instead of this, the resolution offered by Mr. Sachs and
cited above, was unanimously adopted.

An amendment which, Professor Wiley suggested, Mr. Sachs
should include in his resolution, and which amendment would
practically have allowed the use of Professor Wiley's method of
temperature correction as an alternate method, was declined by
Mr. Sachs.

This International Committee, which numbers among its mem-
bers some of the most eminent sugar chemists of Europe, there-

fore certainly did *not* endorse Professor Wiley's method of correction factors, which takes into account an alleged influence of temperature on the specific rotation of sucrose.

This fact alone would seem to cast serious doubt on the validity of the opinion hazarded, "without hesitation," by Professor Wiley, "that the points established by Andrews eleven years ago, are now fully accepted by practically all the investigators of the world."

<div align="right">

F. G. WIECHMANN,

Secretary, The International Committee, etc.

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BOOKS RECEIVED.

The Chemical Analysis of Iron. A complete account of all the best known methods for the analysis of iron, steel, pig-iron, iron ore, limestone, slag, clay, sand, coal, coke, and furnace and producer gases. By Andrew Alexander Blair. Fourth Edition. Philadelphia: J. B. Lippincott Co. 1901. 319 pp. Price, $4.00.

A Compendium of Gold Metallurgy and Digest of U. S. Mining Laws, Water Rights and Desert Land Laws, by E. M. and M. L. Wade, 115½ North Main St., Los Angeles, Cal. 140 pp.

Condimental and Medicinal Cattle and Poultry Foods, Bulletin 132. February, 1901. Connecticut Agricultural Experiment Stations, New Haven, Conn. 7 pp.

Spraying. Bulletin No. 70. November, 1900. 32 pp. Poultry Experiments. Bulletin No. 71. December, 1900. 20 pp. Commercial Fertilizers. Bulletin No. 72. January 1, 1901. 32 pp. West Virginia University Agricultural Experiment Station, Morgantown, W. Va.

The Sunflower Plant: Its Cultivation, Composition, and Uses. By Harvey W. Wiley. Bulletin No. 60, U. S. Department of Agriculture, Division of Chemistry, Washington, D. C. 32 pp.

Pure-food Laws of European Countries, affecting American Exports. Prepared, under the direction of H. W. Wiley, by W. D. Bigelow. Bulletin No. 61, U. S. Department of Agriculture, Washington, D. C. 39 pp.

Experiments on the Effect of Muscular Work upon the Digestibility of Food and the Metabolism of Nitrogen, conducted at the University of Tennessee, 1897 to 1899. By Chas. E. Wait. Bulletin No. 89, U. S. Department of Agriculture, Office of Experiment Stations, Washington, D. C. 77 pp.

First Report on Food Products, for 1900. December, 1900. 61 pp. Fertilizer Analyses and Analyses of Iron Ores. January, 1901. 32 pp. Analyses of Fertilizers. February, 1901. 24 pp. North Carolina State Board of Agriculture, Raleigh, N. C.

Report of the Connecticut Agricultural Experiment Station for the Year

ending October 31, 1900. Part II. Food Products. Connecticut Agricultural Experiment Station, New Haven, Conn. 218 pp.

Milk, 1900. Bulletin No. 74, Laboratory of the Inland Revenue Department, Ottawa, Canada. 13 pp.

An Ephemeris of Materia Medica, Pharmacy, Therapeutics, and Collateral Information. Vol. VI, No. 3. January, 1901. Brooklyn, N. Y. 136 pp.

Nutrition Investigations at the University of Illinois, North Dakota Agricultural College, and Lake Erie College, Ohio, 1896 to 1900.- Bulletin No. 91, U. S. Department of Agriculture, Office of Experiment Stations, Washington, D. C. 1900. 42 pp.

A Manual of Laboratory Physics. By H. M. Tory, M.A., and F. M. Pritcher, M.Sc. New York : John Wiley & Sons. 1901. ix + 288 pages. Cloth, $2.00.

The Soy Bean as a Forage and Seed Crop. By C. S. Phelps. Bulletin No. 22, Storrs Agricultural Experiment Station, Storrs, Conn. 20 pp.

Experiments arranged for Students in General Chemistry. By Edgar F. Smith and Harry F. Keller. Fourth Edition, enlarged, with 41 illustrations. Philadelphia : P. Blakiston's Son & Co. 1900. 88 pp. Price, 60 c.

The American Year-Book of Medicine and Surgery, being a yearly digest of scientific progress and authoritative opinion in all branches of medicine and surgery, drawn from journals, monographs, and text-books, of the leading American and foreign authors and investigators. Under the general editorial charge of George M. Gould, M.D. Vol. I, Medicine. Philadelphia and London : W. B. Saunders & Co. 1901. 681 pp. Cloth, $3.00. Half morocco, $3.75.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

CAMPHOROXALIC ACID DERIVATIVES. VI.

BY J. BISHOP TINGLE.
Received November 10, 1900.

INTRODUCTION.

IN the course of an investigation of the action of ethereal oxalates on aliphatic ketones,[1] it was found that the impure sodium camphor, obtained by the action of one atomic proportion of sodium on camphor, in boiling toluene solution, condenses with ethylic oxalate. The yield waš extremely poor. At that time, the question of the presence in the camphor molecule of the group —$CH_2.CO$— was an open one, and the first conclusive and direct proof of its occurrence was afforded by this work. Apart from the special interest which the subject thus acquired, it possessed other more general ones; hence, the investigation of the above condensation product, termed ethylic camphoroxalate, was continued at the Heriot-Watt College, Edinburgh.

The yield was improved materially and a number of derivatives prepared and studied. Pressure of other work caused the suspension of the research until 1897. During this interval, the point alluded to above, regarding the constitution of camphor, was generally recognized as settled, but other questions had arisen that appeared to make the extended investigation of camphoroxalic acid desirable. One of these concerned the true constitution of "diketones," of which ethylic camphoroxalate may be taken as an example : were they to be regarded as unsaturated

[1] Inaugural Dissertation., Munich University, 1889, p. 34.

keto-alcohols or as true diketones? From the almost neutral character of the camphor nucleus, and its relatively large mass, camphoroxalic acid appeared to be peculiarly well fitted for the purpose of investigation in this direction. A further object was to accumulate data which might elucidate to some extent the mechanism of the Claisen condensation. The work was therefore resumed at the University of Chicago, and has since been continuously prosecuted, first at the University of Pennsylvania, and subsequently in this laboratory. The results as regards the constitution of camphoroxalic acid are apparently complete, and indicate that it is an unsaturated keto-alcohol. In addition to this, a new class of compounds has been discovered, formed by the condensation of the acid with amines. Most of the observations which have been made have been published at intervals as the work proceeded ; in the present paper, thèse scattered communications[1] are briefly coordinated, corrected where necessary, and a description is given for the first time of a series of compounds obtained by the action of camphoroxalic acid and ethyl camphoroxalate on ammonia and certain aliphatic amines.

THEORETICAL.

A number of experiments were made in order to determine the most suitable conditions for the preparation of camphoroxalic acid and its ethyl salt ; these may be thus summarized : (1) Sodium with ethyl oxalate and camphor in boiling toluene ; (2) Dried sodium ethoxide suspended in boiling ether; (3) Sodium ethoxide in absolute alcoholic solution; (4) Sodium wire with the camphor and ethyl oxalate in absolute ethereal solution ; (5) Sodium wire as in 4, in dried, light petroleum solution. The results are as follows :

Experiment.	Molecules camphor to 1 molecule ethyl oxalate.	Atoms sodium.	Crude ethyl salt and acid per cent. of theoretical.	Acid formed per cent. of theory.	Acid 1 part : of ethyl salt.
1	2	2	small	....	....
2	1	1	10	....	....
3	1	1	4.4	....	....
4	1¼	1	58.0	4.9	0.07
5a	1¼	1	63.5	Ethylic salt only	
5b	1½	1	92.4	17.0	0.2
5c	2	2	66.5	44.6	1.8

[1] Inaug. Diss., Munich, 1889, p. 34 : *J. Chem. Soc.* (London), 1890, 652 ; *Am. Chem. J.,* 19, 393 (1897) ; *Ibid.,* 20, 318 (1898) ; *Ibid.,* 21, 238 (1899) ; *Ibid.,* 23, 214 (1900).

It is immediately evident that the first three methods are quite unsuited for the preparation of the acid on a large scale. Experiments 4 and 5 show that the use of light petroleum is more favorable to the yield than that of ether, probably because of its higher boiling-point (about 70°) ; its cheapness, and the ease with which it can be dehydrated are also incidental, but highly important advantages. The influence of the varying amount of sodium is illustrated in experiments 5*a*, *b*, and *c*, the total yield is improved by the use of 1 atom to 1½ molecules of camphor, but a larger proportion of the latter favors the formation of acid at the expense of ethylic salt.

Recent research appears to indicate that, except in the case of hydrocarbons of the acetylene type, or those containing the linkage *C:C.C.C:C.*,[1] none of the organo-metallic compounds have the metal directly linked with carbon ; accordingly, in formulating the above facts, Claisen's explanation of his condensation requires some modification. The figures in the above table show that the action of sodium on camphor is by no means complete, but it may be represented as follows :

(1.) $2C_8H_{14}\diagup\!\!\!\!\diagdown{\overset{CH_2}{\underset{CO}{|}}} + 2Na \longrightarrow$

$$C_8H_{14}\diagup\!\!\!\!\diagdown{\overset{CH}{\underset{C.ONa}{||}}} + C_8H_{14}\diagup\!\!\!\!\diagdown{\overset{CH_2}{\underset{CH.ONa}{|}}}$$

(Sodium camphor.) (Sodium borneol.)

(2.) $C_8H_{14}\diagup\!\!\!\!\diagdown{\overset{CH}{\underset{C.ONa}{||}}} + C_2H_5.O.CO.CO.OC_2H_5 \longrightarrow$

$$C_2H_5.O.CO.C\diagup\!\!\!\!\diagdown{\overset{ONa}{\underset{OC_2H_5}{}}}OC_{10}H_{15}.$$

(3) $C_2H_5.O.CO.C\diagup\!\!\!\!\diagdown{\overset{ONa}{\underset{OC_2H_5}{}}}OC_{10}H_{15} + {\overset{H_2C}{\underset{OC}{|}}}\diagdown C_8H_{14} \longrightarrow$

$${\overset{OC}{\underset{C_2H_5.O.CO.CONa:C}{|}}}\diagdown C_8H_{14} + C_{10}H_{16}O + C_2H_5O .$$
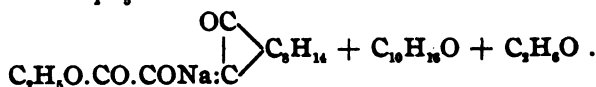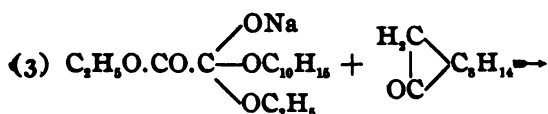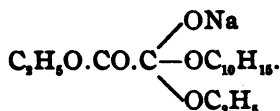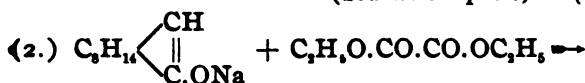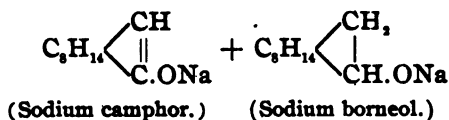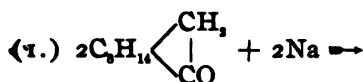
The sodium salt when acidified yields the ketone directly.

[1] J. Thiele : *Ber. d. chem. Ges.*, **34**, 69 (1901).

The large amount of acid produced and the conditions which have been shown to favor its formation, prove that this cannot be ascribed to hydrolysis of the ethyl salt, either while the borneol and excess of camphor are being extracted, or as the result of traces of moisture in the apparatus. The idea that the borneol and camphor mechanically retain ethyl salt sufficient to yield, by subsequent hydrolysis, the amount of acid actually obtained, is also not supported by the comparative experiments. With the modifications already suggested, Brömme & Claisen's explanation of the formation of acetophenone oxalic acid may be accepted.[1] According to this the compound formed, as represented in the second equation, combines either with a second molecule of sodium camphor, or with one of sodium ethoxide, this last being produced from the alcohol eliminated in the third phase of the reaction:

$$(4).\quad C_{10}H_{15}O\overset{NaO}{\underset{C_2H_5O}{\diagdown}}C.CO.OC_2H_5 + RONa \longrightarrow$$

$$C_{10}H_{15}O\overset{NaO}{\underset{C_2H_5O}{\diagdown}}C.C\overset{ONa}{\underset{OR}{\diagup}}OC_2H_5.$$
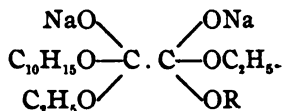
By the interaction of camphor as in equation 3, we get the salt
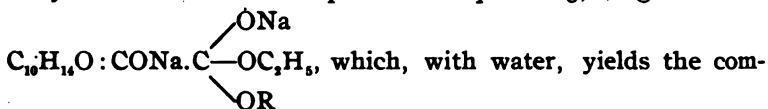
$$C_{10}H_{14}O:CONa.C\overset{ONa}{\underset{OR}{\diagup}}OC_2H_5,$$ which, with water, yields the compound $C_{10}H_{14}O : CONa.CO.ONa + C_2H_6O + ROH$ $(R = C_2H_5$ or $C_{10}H_{15}$). It must be confessed that this explanation is not wholly satisfactory, as it affords no very obvious reason for the failure of the ortho carbon atom in the above compound
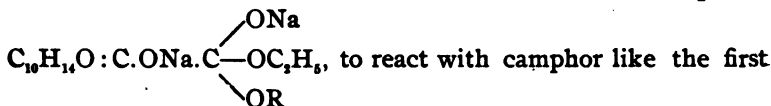
$$C_{10}H_{14}O:C.ONa.C\overset{ONa}{\underset{OR}{\diagup}}OC_2H_5,$$ to react with camphor like the first one in equation 3, and yield, eventually, dicamphoroxalyl, $C_{10}H_{14}O : COH.COH : OC_{10}H_{14}$. Hitherto, none of this substance has been found, although attempts have been made to prepare it; therefore, the inference is, either that it is hydrolyzed during the extraction of the acid, or that the experimental conditions are

[1] *Ber. d. chem. Ges.*, **21**, 1132.

unfavorable for its production. A similar lack of success was experienced in an attempt to obtain the corresponding acetone derivative from ethyl camphoroxalate and acetone in the presence of sodium. An attempt which was made to test the above theory was based upon the following considerations: The symmetry of ethyl oxalate precludes the formation of more than one camphoroxalic acid, apart from possible stereoisomers, but an unsymmetrical dibasic ester should yield two structurally different acids according to which of the original carbethoxyl groups reacted; this is illustrated by the following equations, in which the carbon atoms of the carbethoxyl groups are distinguished as 1 and 2; $(R = C_2H_5$ or $C_{10}H_{15}$; $R'' = C_8H_{14} : CO)$.

The additive compound $NaO.\overset{1}{C}(OR)_2 \ldots \overset{2}{C}(OR)_2.ONa$ of equation 4 would become successively

(a) $NaO.\overset{1}{C}:CR'' \ldots \overset{2}{C}(OR)_2.ONa$ or $NaO.\overset{1}{C}(OR)_2 \ldots \overset{2}{C}.ONa :$ CR'';

(b) $NaO.\overset{1}{C} : CR'' \ldots \overset{2}{C} : O.ONa$ or $NaO.\overset{1}{C}O \ldots \overset{2}{C}.ONa : CR''$;

(c) $HO.\overset{1}{C} : CR'' \ldots \overset{2}{C}O.OH$ or $HO.\overset{1}{C}O \ldots \overset{2}{C}.OH : CR''$.

Pyrotartaric acid, $HO.OC.CH(CH_3).CH_2.CO.OH$, is perhaps the simplest acid fulfilling the conditions necessary to test the above hypothesis, and experiments were made with it. *Diethyl pyrotartrate* is readily prepared by E. Fischer's method, and the yield is excellent. Sodium wire dissolves slowly in a light petroleum solution of camphor and ethyl pyrotartrate; the condensation product which was finally isolated, gave a red coloration with ferric chloride and alcohol, but no acid could be obtained from it by hydrolysis. The yield of condensation product was small, and was not improved by the varying conditions employed. In pursuit of the same object *ethyl oxalacetate* was employed instead of the ethyl pyrotartate. The product was a syrup having a yellowish brown color in ethereal solution; in aqueous solution, a blue-purple coloration is produced on the addition of a little mineral acid; with a larger excess, the color is discharged; alkalies change it to deep red. When hydrolyzed, the compound yields a liquid acid which readily liberates carbonic anhydride from carbonates; an attempt to induce it to crystallize, after purification by means of the barium salt, was unsuccessful. The compound is probably a condensation product

of ethyl oxalacetate similar to those described by Claisen[1] alone, and in conjunction with Hare,[2] and by Ruhesmann and Hemmy.[3]

Camphoroxalic Acid is readily soluble in ether and benzene, moderately so in light petroleum, and sparingly in water ; it is preferably purified by recrystallization from light petroleum, being deposited in large, well-developed six-sided monoclinic plates, resembling those of quartz in appearance, and melting at 88°. When quickly distilled under the ordinary pressure some camphor is produced, but the greater portion of the acid passes over unchanged. Prolonged exposure to a temperature of 150° failed to yield any isomeric compound (cf. pp. 377). When heated with barium hydroxide, in a current of dry purified hydrogen, hydrolysis occurs at the position of the ethylene linkage, and camphor and barium oxalate are formed. No physiological action is produced on a dog by the intravenous injection of 0.241 gram of sodium camphoroxalate per kilo of body weight. The *copper, silver, calcium, lead, and barium salts* are sparingly soluble and amorphous ; the first is green, the second slightly yellow, and the remainder white. The *sodium salt*, which is very readily soluble, rapidly decolorizes potassium permanganate at the ordinary temperature. When reduced by means of sodium amalgam the acid yields a *lactone*, C_8H_{14} $\begin{array}{l}\diagup CH.CH.OH.CO \\ | O \\ \diagdown CH \underline{}\end{array}$, which is deposited from ether as an unctuous solid, melting at 75°–76°. The action of *bromine* on camphoroxalic acid was studied in the hope that it might yield evidence of the presence or otherwise of an ethylene linkage, and also because, by its means, it appeared possible that an isomeric acid might be produced. The substances react either in chloroform solution, or when bromine vapor is brought into contact with the dry acid ; hydrogen bromide is eliminated more quickly in the former than in the latter case, and the product is an oil which crystallizes with difficulty, cannot be completely purified, and contains bromine. It gives no coloration with ferric chloride and alcohol, and when reduced with magnesium amalgam yields an acid closely resembling camphoroxalic acid in general properties but differing from it in crystallographic form. These results may be explained in one of two

[1] *Ber. d. chem. Ges.*, **24**, 130.
[2] *Ibid.*, **24**, 120.
[3] *J. Chem. Soc.*, **71**, 334 (1897).

ways : If the ethylene linkage is attacked, the additive compound

would be $C_8H_{14}\diagup\diagdown$ with $\genfrac{}{}{0pt}{}{CBr.CBr.OH.CO.OH}{|}{CO}$; this should readily elim-

inate hydrogen bromide and yields either the compound

$C_8H_{14}\diagup\diagdown\genfrac{}{}{0pt}{}{CBr.CO.CO.OH}{|}{CO}$, or $C_8H_{14}\diagup\diagdown\genfrac{}{}{0pt}{}{C:COBr.CO.OH}{|}{CO}$; on reduc-

tion the former would give the diketonic acid,

$$C_8H_{14}\diagup\diagdown\genfrac{}{}{0pt}{}{CH.CO.CO.OH}{|}{CO}\ ,$$
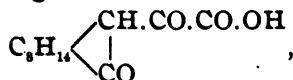
and the latter camphoroxalic acid. On the other hand it is well-known that camphor itself very readily combines with bromine, forming the dibromide $C_{10}H_{16}Br_2O$, which easily eliminates hydrogen bromide and is converted into bromocamphor, $C_{10}H_{15}BrO$; if the nucleus of camphoroxalic acid acts in a similar manner, then, by the reduction of this bromo acid, an isomeric camphoroxalic acid should be formed which should not differ materially from the ordinary compound in properties, and should give a similar red coloration with ferric chloride, while the keto acid could not do so. This second view of the reaction appears at present to be the more probable.

When heated with hydrochloric acid, or with dilute sulphuric acid (1 : 3), camphoroxalic acid yields a little oxalic acid, but by far the larger proportion of it is converted, by the addition of the elements of 2 mols. water, into an *acid* which crystallizes with some difficulty in granular nodules melting at 92°–93°. This compound, $C_{12}H_{20}O_6$, differs from the parent substance by its sparing solubility in light petroleum; the production of a deep blue coloration with ferric chloride and alcohol, and by its failure to give a precipitate with calcium chloride in ammoniacal solution.

The action of acetic anhydride on camphoroxalic acid is complex, and although much time and labor have been spent on its study, the results cannot be considered satisfactory. This arises from the fact that under the most favorable circumstances the yields are poor, and very slight alterations in the experimental conditions cause the acid to undergo complete decomposition. The purity of the anhydride employed is a most important factor. Three compounds have been isolated, the first is *acetylcamphor-*

$$\text{oxalic acid, } C_8H_{14}\diagdown\genfrac{}{}{0pt}{}{C : C(O.CO.CH_3).CO.OH}{\underset{CO}{\big|}}$$
which is also

formed by the interaction of the anhydride and ethyl camphor-oxalate ; it crystallizes from a mixture of benzene and light petroleum in reticulated stellate needles, melting at $133.5°-134.5°$. The second compound is also formed by the action of benzoyl chloride on camphoroxalic acid ; it gives no coloration with alco-hol and ferric chloride, is insoluble in sodium hydroxide solution, and crystallizes in colorless slender needles melting at $192°-193°$. Bromine and hydroxylamine are both without action on the com-pound to which the formula

$$C_8H_{14}\diagdown\genfrac{}{}{0pt}{}{CO}{\underset{CH.C}{\big|}}$$
$$O\diagdown\big|\diagup O$$
$$C_8H_{14}\diagdown\genfrac{}{}{0pt}{}{CH.C}{\underset{CO}{\big|}}$$
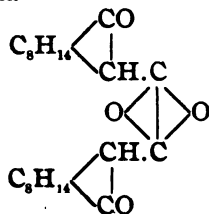
is, at least provisionally, assigned.   The   third compound is formed with great difficulty, and all attempts to improve the yield were fruitless.   It crystallizes in small, slender, colorless needles which darken at about $240°$, and melt at $242°$.   It does not react with bromine in chloroform solution, while aqueous sodium hydroxide dissolves a portion and turns the remainder yellow.   The formula

$$C_8H_{14}\diagdown\genfrac{}{}{0pt}{}{CO}{\underset{C:C}{\big|}}$$
$$O\diagdown\diagup CO$$
$$C_8H_{14}\diagdown\genfrac{}{}{0pt}{}{C:C}{\underset{CO}{\big|}}$$
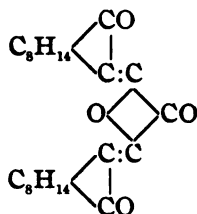
is in harmony with the little which is known of the substance.

Acetylcamphoroxalic acid readily reacts with bromine either in the form of vapor, or in chloroform solution; in both cases hydro-gen bromide is copiously evolved, but no crystalline product could be isolated.   The result confirms the explanation offered above of the action of bromine on camphoroxalic acid itself, and there appears little room for doubt that the haloid attacks the camphor nucleus of both compounds.

With benzoic anhydride, and camphoroxalic acid, no definite results could be obtained ; at 110° benzoic acid sublimed, and at 150° carbonic anhydride was evolved.

Phenylhydrazine and camphoroxalic acid, in anhydrous ethereal solution, yield a salt which crystallizes in minute colorless needles, darkens at 205°, and melts and evolves gas at 214°–215°.

A somewhat extensive study has been made of the condensation compounds of camphoroxalic acid and amines, both of the aromatic and aliphatic series.   The primary products in all cases are apparently simply additive substances of the type

$$C_8H_{14} \Big\langle \begin{array}{l} CH.C.OH.CO.OH \\ | \quad | \\ CO \ NHR \end{array}$$
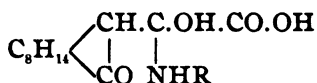
but only one body of this formula has been isolated, that obtained from hydroxylamine : the remainder appear to be unstable, and eliminate the elements of water, giving rise to products of the general formula

$$C_8H_{14} \Big\langle \begin{array}{l} C : C.CO.OH \\ | \quad | \\ CO \ NHR \end{array}$$
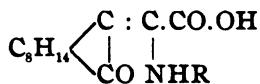
Compounds of this nature have been prepared from ammonia, semicarbazine,[1] aniline, and α- and β-naphthylamine.   These substances may then undergo furthei change ; in the case of the aniline derivative carbonic anhydride is evolved ; the hydroxylamine compound, mentioned above, loses the elements of two molecules of water and yields an isoxazole, while orthophenylene-diamine condenses directly with the acid to form a quinoxaline derivative.   The above series of compounds might be formulated in various other ways; perhaps one of the most plausible is

$$C_8H_{14} \Big\langle \begin{array}{l} CH.C.CO.OH \\ | \quad \| \\ CO \ NR \end{array}$$
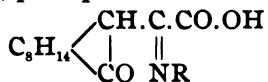
the three chief reasons for preferring the first formula are: (1) The stability of the compounds toward alkalies; (2) The fact that with all reagents that have been successfully tried, and which could afford crucial tests, both camphoroxalic acid, and ethyl camphoroxalate act as hydroxy-unsaturated compounds ; hence, analogy is strongly in favor of adopting the same view in any

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[1] It appears preferable to the writer to designate the compound $NH_2.CO.NH.NH_2$, *semicarbazine*, in analogy with phenylhydrazine.

doubtful cases; (3) There is some direct evidence of the existence, in the above compounds, of the imido group, and in the case of the ammonium derivative, of the amido radical. On the other hand, there has been complete failure to obtain similar derivatives of secondary amines, either aliphatic or aromatic, and, except on stereochemical grounds, this is not readily explicable by the first formula, but is easily understood from the second one. It is hoped that subsequently further light may be obtained on the subject.

In naming the compounds the simplest and most advisable plan appeared to be to regard them as derived from the complex

$$C_8H_{14}\left\langle\begin{array}{l} C:CH_2 \\ | \\ CO \end{array}\right. ,$$
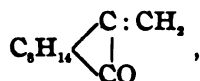
for which the term *camphoformene* suggests itself; it is self-explanatory and indicates the presence of the double linkage.

By the action of ammonia on sodium or potassium camphor-oxalate, in alcoholic solution, at 100° under pressure, *sodium camphoformeneamine carboxylate* is obtained, from which the free acid,

$$C_8H_{14}\left\langle\begin{array}{ll} C:CH.CO.OH \\ | \quad | \\ CO \; NH_2 \end{array}\right. ,$$

is readily liberated. It crystallizes in colorless plates, melts, and evolves gas at 178°, is not soluble in light petroleum, and gives no coloration with ferric chloride and alcohol. The acid dissolves readily in hot, but not in cold, sodium carbonate solution, and is reprecipitated on acidification ; by means of the diazo reaction it regenerates camphoroxalic acid. An attempt to prepare campho-formeneamine by heating the acid was unsuccessful ; absolute alcoholic ammonia and free camphoroxalic acid yield, as chief product, ammonium camphoroxalate, which is crystalline, and melts and evolves gas at about 212°.

Sodium camphoroxalate combines with hydroxylamine in concentrated aqueous-alcoholic solution, at the ordinary temperature, forming the compound

$$C_8H_{14}\left\langle\begin{array}{ll} CH.C.OH.CO.OH \\ | \quad | \\ CO \; NH.OH \end{array}\right.$$

This crystallizes in bushy clusters of colorless, lustrous needles, which sometimes appear flattened into plates; it melts and

evolves gas at 146.5°. No alkaline fumes are evolved when the compound is boiled with sodium hydroxide solution, and no coloration is produced with alcohol and ferric chloride. That this additive compound is represented by the above formula, and not by the possible alternative one,

$$C_8H_{14}\Big\langle \begin{matrix} C(NH.OH).CH.OH.CO.OH \\ | \\ CO \end{matrix}$$
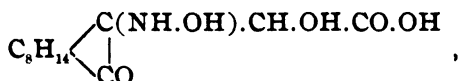
is proved by the production of *camphylisoxazole*,

$$C_8H_{14}\Big\langle \begin{matrix} C-CH \\ \| \quad \| \\ C \quad N \\ \diagdown O \diagup \end{matrix}$$
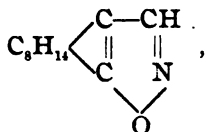
when the additive compound is treated with a mixture of glacial acetic acid and acetic anhydride. The isoxazole crystallizes in colorless, lustrous needles, which melt at 124°–125°. At about 70° it sublimes slowly, and forms very slender, silky, long needles; no coloration is produced with concentrated nitric acid.

Semicarbazine combines with camphoroxalic acid under the same conditions as hydroxylamine, and also in alcoholic solution, under pressure, at 100°. The product consists of two compounds which are separated by means of ether. The more soluble one crystallizes from acetone in small white needles, melting and decomposing at 218°. The second compound is insoluble in all ordinary neutral organic media ; it is purified by means of glacial acetic acid and alcohol, and is deposited in microscopic needles— aggregated into cubical clusters ; these melt and decompose at 209°–210°. Both compounds dissolve in sodium carbonate solution with equal readiness; the first is reprecipitated in a gelatinous condition, but after drying, its melting-point is unchanged. The' solution of the second compound is also precipitated by acids, but the precipitate shows the same melting-point as the "soluble" body. Identical results are obtained by the elementary analysis of the two substances. It would be easy to suggest possible explanations of the above phenomena, but it appears better to abstain from doing so until more experimental information is forthcoming.

Aniline and camphoroxalic acid yield three compounds, one of these, *phenylcamphoformeneamine carboxylic acid,*

$$C_8H_{14}\diagdown\begin{matrix} C : C.CO.OH \\ | \quad | \\ CO\ NH.C_6H_5 \end{matrix}\,,$$
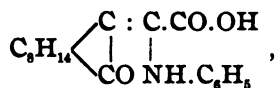
corresponds with the ammonia derivative of camphoroxalic acid, and is formed by boiling aniline with sodium camphoroxalate in aqueous alcoholic solution; it crystallizes in bright yellow needles, and melts and decomposes at 174°. The second compound,

$$C_8H_{14}\diagdown\begin{matrix} C : C.CO.ONH_3C_6H_5 \\ | \quad | \\ CO\ NH.C_6H_5 \end{matrix}\,,$$
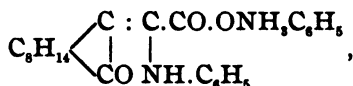
is the *aniline salt* of the preceding acid, and is formed by warming for a few moments on the water-bath, a mixture of aniline and camphoroxalic acid in concentrated benzene solution. It crystallizes from benzene on the addition of light petroleum, in small, colorless needles which melt and decompose at 158°. The salt is stable at the ordinary temperature in the absence of moisture and acid vapors; when cautiously heated below its melting-point, it is resolved into aniline and phenylcamphoformeneamine carboxylic acid, and the same change is produced immediately by dilute sulphuric acid, hydrochloric acid, alkalies, and more slowly, by water. Rapid heating above its melting-point results in the production of aniline, carbonic anhydride, and phenylcamphoformeneamine (see below). Prolonged boiling with concentrated alkali, aqueous or alcoholic, converts the carboxylic acid, and therefore, of course, the aniline salt, into aniline and the alkali salt of camphoroxalic acid.

The third compound from aniline and camphoroxalic acid is formed by heating either of the preceding substances above their melting-points, and also by the direct action of the constituents at 130°. Its preparation and reactions characterize it as *phenylcamphoformeneamine*,

$$C_8H_{14}\diagdown\begin{matrix} C : CH \\ | \quad | \\ CO\ NH.C_6H_5 \end{matrix}$$
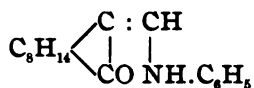
It crystallizes in colorless, rhombic plates, and occasionally in characteristic slender hair-like needles, upwards of an inch in length. With bromine, it forms a *hydrobromide*, while hydro-aurochloric acid and hydroplatinochloric acid yield *salts*, of which the former is very unstable. Prolonged boiling with concentrated alkali is without effect on the compound. With acetic anhydride an unstable crystalline derivative is obtained which melts at 134°.

Benzoyl chloride reacts with the amine, yielding crystals resembling those of potassium nitrate in shape, and melting at 160–161°. The derivative formed by the action of phenyl-sulphonic chloride is crystalline, melts at 133°, and does not dissolve in sodium hydroxide solution. With methyl iodide, the amine apparently does not react.

α-Naphthylamine reacts with sodium camphoroxalate under somewhat similar conditions to aniline and forms *α-naphthyl-camphoformeneamine carboxylic acid*,

$$C_8H_{14} \left\langle \begin{matrix} C : C.CO.OH \\ | \quad | \\ CO\ NH.C_{10}H_7 \end{matrix} \right. ,$$

which crystallizes with $\frac{1}{2}$ mol. C_6H_6 in well developed, transparent, amber-colored prisms, melting at 170°. At a little above 100°, the crystals lose their benzene and change to a brown powder which also melts at 170°. The corresponding *derivative* of *β-naphthylamine* is deposited from benzene or toluene in bright yellow needles which melt and decompose at 173°. From neither of these compounds has it hitherto been possible to obtain a naphthyl camphoformeneamine, corresponding with the phenyl-derivative. The pronounced color—bright yellow to brown,— of these three carboxylic acids suggests the possibility, that instead of being represented by the formula

$$C_8H_{14} \left\langle \begin{matrix} C : C.CO.OH \\ | \quad | \\ CO\ NH.R \end{matrix} \right. ,$$
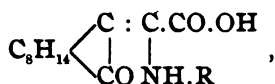
they, in reality, possess a "betaine" structure,

$$C_8H_{14} \left\langle \begin{matrix} C : C . CO \\ | \quad | \quad | \\ | \quad | \quad O. \\ CO\ NH_2 \end{matrix} \right.$$
$$R$$
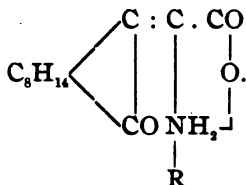
The interaction of orthophenylenediamine and camphoroxalic acid, carried out under similar conditions to those employed for the preparation of the preceding carboxylic acids, results in the production of *camphoquinoxaline*, $C_{18}H_{20}N_2O_2$; it crystallizes in bright yellow needles, melts at 246°, and dissolves in concentrated sulphuric acid, giving a color resembling that produced by potassium chromate in the same circumstances. Under conditions

which preclude the idea of hydrolysis, ethylic camphoroxalate and orthophenylenediamine yield a substance identical with that from the acid. The compound may be represented by one or other of the formulae:

$$(1)\ C_8H_{14}\begin{array}{c}C\ :\ C—CO\\ |\quad |\quad |\\ CO\ NHNH\\ \diagdown\diagup\\ C_6H_4\end{array}\ ;\quad (2)\ C_8H_{14}\begin{array}{c}C\ :\ C—C.OH\\ |\quad |\quad ||\\ CO\ NHN\\ \diagdown\diagup\\ C_6H_4\end{array}\ ;$$

$$(3)\ C_8H_{14}\begin{array}{c}CH.C—CO\\ |\quad ||\quad |\\ CO\ N\ NH\\ \diagdown\diagup\\ C_6H_4\end{array}\ ;\quad (4)\ C_8H_{14}\begin{array}{c}CH.C—C.OH\\ |\quad ||\quad ||\\ CO\ N\ N\\ \diagdown\diagup\\ C_6H_4\end{array}$$
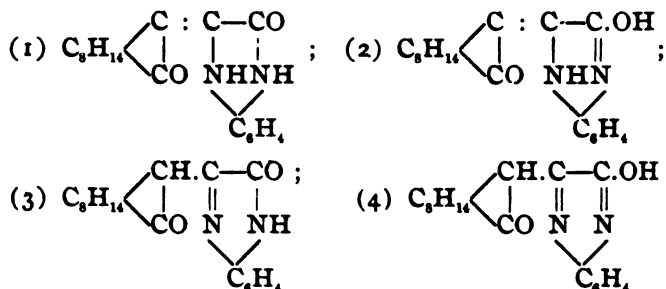
The relationship of formulae 1 and 2 to 3 and 4 respectively, is that of a lactam to the corresponding lactim; excluding this aspect of the question as involving the broader one of the constitution of the quinoxalines, sodium camphoroxalate should give the compound having the second formulae, while ethylic camphoroxalate should yield that represented by the first one. Hence it must be concluded, either that the first compound is unstable and changes spontaneously into the second, or that the sodium salt of the second, after acidification, changes to the first; at present, this latter suggestion appears to be the more probable, unless, of course, the case is one of tautomerism in the strict sense of the term.

ETHYL CAMPHOROXALATE.

The crude condensation product of ethyl oxalate and camphor always contains ethyl oxalate, and although this is of little consequence for some purposes, a supply of pure substance is, of course, highly desirable and occasionally absolutely necessary. The crude ethyl salt does not react with copper acetate either in neutral, or ammoniacal solutions, irrespective of whether the ester is dissolved in water, ether, or light petroleum. The compound thus exhibits a striking contrast to formylcamphor, which is a strong acid. When boiled, a portion suffers decomposition and part is volatilized unchanged. An attempt to separate the mixed ethyl salts by systematic treatment with sodium hydroxide, sodium carbonate, and sodium hydrogen carbonate solutions, resulted only in the hydrolysis of the compounds. It

was ultimately found to be most convenient to hydrolyze the crude ester, and then esterify the purified camphoroxalic acid by a modification of E. Fischer's method. The compound is deposited from light petroleum in fern-like aggregates, consisting of long needles, melting at 40.5°. It is miscible with ether in all proportions, and is extremely readily soluble in ordinary media, with the exception of light petroleum. With alcohol and ferric chloride solution a deep red coloration is obtained. Fractional esterification failed to show any lack of homogeneity in camphoroxalic acid (cf. pp. 368).

Bromine and ethylic camphoroxalate readily react, hydrogen bromide being evolved; when the two are heated in chloroform solution oxalic acid is formed, but at the ordinary temperature the product was an oil which refused to crystallize.

With acetic anhydride the ester yields acetylcamphoroxalic acid, as already described (cf. p. 369). No derivative could be obtained by the action of either benzoyl chloride or benzoic anhydride, in spite of considerable variation of the experimental conditions. The greater relative stability of the ethylic salt, as compared with camphoroxalic acid, towards these reagents, is interesting, and supports the view that the acid, under their influence, undergoes deep-seated changes involving the carboxyl group.

Carefully dried ammonia produces a white precipitate when passed into a well cooled absolute alcoholic solution of ethylic camphoroxalate; the substance is unstable, and is resolved spontaneously into its constituents. It is doubtless an additive compound with the formula

$$C_8H_{14} \underset{\diagdown CO \ NH_2}{\overset{\diagup CH.C(OH).CO.OC_2H_5}{\big\langle}}$$
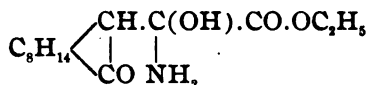
When heated at 100°, with alcoholic ammonia in excess, it is converted into *camphoformeneaminecarboxylamide*,

$$C_8H_{14} \underset{\diagdown CO \ NH_2}{\overset{\diagup C : C.CO.NH_2}{\big\langle}},$$

which is also formed directly by the interaction of ammonium chloride, potassium hydroxide, and ethylic camphoroxalate under the same conditions. It crystallizes in colorless microscopic needles, melting at 227°–228°. Boiling with sodium hydroxide solution causes the regeneration of ammonia and camphoroxalic acid.

A compound which melted at 225°, and was previously[1] obtained
by the action of dry ammonia on ethyl camphoroxalate in
absolute ethereal solution, was prepared from the crude ethylic
salt, containing, therefore, ethyl oxalate, and was almost
certainly oxamide.

In the first paper on this subject,[2] a substance was described
which was produced by the interaction of crude ethyl camphor-
oxalate and hydroxylamine; it crystallized in silky needles, and
melted at 193°. From its melting-point and general properties,
the compound is probably oxalenediamidoxime $OH.N:C(NH_2)$.
$C(NH_2):N.OH$; in any case it is not a derivative of ethyl cam-
phoroxalate, as all attempts to obtain it from the pure compound
were fruitless. Experiments with the ethyl salt and hydroxyl-
amine at 100° led to no definite results, but at the ordinary tem-
perature a product is formed which crystallizes in colorless,
slender needles, melting at 120°–121°. Its nature has not yet
been investigated.

Methylamine and ethyl camphoroxalate readily condense at
100°, under conditions similar to those employed in the case of
ammonia. The product is deposited in small, white needles which
melt at 130° ; it is not very stable, and spontaneously evolves
methylamine, but there is no doubt that it is *methyl campho-
formeneaminecarboxylmethylamide*,

$$C_8H_{14}\begin{cases} C : C.CO.NH.CH_3 \\ | \quad | \\ CO \; NH.CH_3 \end{cases}.$$

Ethyl camphoformeneaminecarboxylethylamide,

$$C_8H_{14}\begin{cases} C : C.CO.NH.C_2H_5 \\ | \quad | \\ CO \; NH.C_2H_5 \end{cases},$$
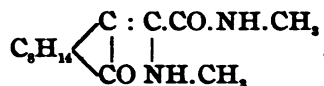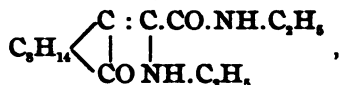
is formed from ethylamine in a similar manner to the preceding
compound, which it resembles in general properties; it crystallizes
in colorless needles, melts at 148°, and very slowly evolves ethyl-
amine. Semicarbazine condenses with ethyl camphoroxalate,
either at the ordinary temperature, or at 100°, forming *ethyl
semicarbazylcamphoformeneaminecarboxylate*,

$$C_8H_{14}\begin{cases} C : C.CO.OC_2H_5 \\ | \quad | \\ CO \; NH.NH.CO.NH_2 \end{cases},$$

[1] *Am. Chem. J.*, **20**, 332 (1898).
[2] *J. Chem. Soc.* (London), **57**, 655 (1890).

which crystallizes in colorless needles, melting at 202°. Molecular weight determinations agree with the formula given. Accompanying this compound a second was sometimes obtained in small quantity which also crystallized in colorless needles, melted at 225°, and may possibly be semicarbazine sulphate.

Ethyl camphoroxalate forms two compounds with aniline. The one, *ethyl phenylcamphoformenecarboxylate*,

$$C_8H_{14} \begin{cases} C : C.CO.OC_2H_5 \\ CO \ NH.C_6H_5 \end{cases},$$
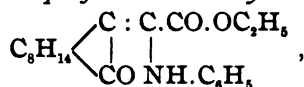
is prepared from its constituents, at 100°, and is deposited in almost white, microscopic, needle-shaped crystals, melting and decomposing at 158°–160°. When hydrolyzed by means of alkalies it yields the corresponding *acid*, m. p. 174, the preparation of which from aniline and sodium camphoroxalate has been already described (cf. p. 374). The second condensation product of aniline and ethyl camphoroxalate is obtained by heating these substances together at 130°; it consists of *phenylcamphoformeneaminecarboxylicanilide*,

$$C_8H_{14} \begin{cases} C : C.CO.NH.C_6H_5 \\ CO \ NH.C_6H_5 \end{cases},$$
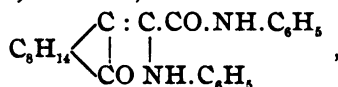
which crystallizes in small, colorless needles, melting at 193°. The compound is not changed by admixture with bromine in chloroform solution, nor by prolonged boiling with aqueous or alcoholic sodium hydroxide. Treatment with sulphuric acid readily gives rise to resinous products. An unstable *platinochloride* appears to be formed, but hydroaurochloric acid quickly undergoes reduction when mixed with the anilide. In the first paper on this subject it was stated that aniline and ethyl camphoroxalate yield oxanilide; this is incorrect as the foregoing account shows. At the time that the statement was made pure ethyl camphoroxalate had not been prepared, and the mistake arose from the use of crude material containing ethyl oxalate. Unfortunately the error has been copied into Morley & Muir's edition of "Watts' Dictionary of Chemistry."

β-Naphthylamine and ethyl camphoroxalate yield, at 100°, *ethyl β-naphthylcamphoformeneaminecarboxylate*,

$$C_8H_{14} \begin{cases} C : C.CO.OC_2H_5 \\ CO \ NH.C_{10}H_7 \end{cases},$$
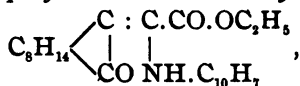
which closely resembles the corresponding phenyl derivative in appearance, and crystallizes in colorless, microscopic needles, softening at about 160°, and melting and decomposing at 174°. The exact melting-point is largely dependent on the rapidity with which the bath is heated. Hitherto, no naphthalide has been obtained corresponding to the " anilide " described above.

The condensation of orthophenylenediamine and ethyl camphoroxalate, leading to the production of camphoquinoxaline, has been described in connection with camphoroxalic acid (p. 375).

Phenylhydrazine and ethyl camphoroxalate, in equimolecular proportion, readily react when boiled in anhydrous ethereal, or light petroleum solution. The product is sparingly soluble, and comparatively stable towards aqueous sodium hydroxide at the ordinary temperature, but gives a deep blue-purple coloration with concentrated nitric acid. It crystallizes in slender, small, white needles, which melt sharply at 212°. A trace of impurity depresses this value very considerably; hence the incorrect melting-point (187°–188°) given in the first paper. The proof that this compound is a *phenylhydrazide*,

$$C_8H_{14} \begin{cases} C : C.CO.OC_2H_5 \\ | \quad | \\ CO \; NH.NH.C_6H_5 \end{cases},$$
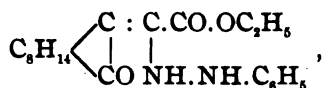
and not a *phenylhydrazone*,

$$C_8H_{14} \begin{cases} CH.C.CO.OC_2H_5 \\ | \quad \| \\ CO \; N.NH.C_6H_5 \end{cases},$$
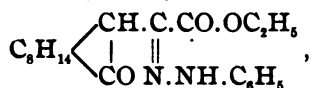
is afforded by its oxidation to *ethyl camphoroxalateazobenzene*,

$$C_8H_{14} \begin{cases} C : C.CO.OC_2H_5 \\ | \quad | \\ CO \; N:N.C_6H_5 \end{cases}.$$
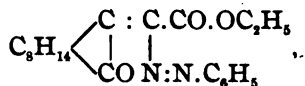
which crystallizes in red needles, melts at 210°, and is much more readily soluble in ether than the phenylhydrazide. The oxidation may be accomplished by means of mercuric oxide in the presence of absolute alcohol, but is preferably carried out by the help of hydrogen peroxide at the ordinary temperature in ethereal solution. The proof of the constitution of this compound affords a strong argument, by analogy, in favor of that assigned to the other condensation compounds described in the preceding pages.

Ethyl camphylphenylpyrazolcarboxylate,

$$C_8H_{14} \diagup \begin{matrix} C-C.CO.OC_2H_5 \\ \| \quad \| \\ C \quad N \end{matrix} \diagdown$$
$$\diagdown\diagup$$
$$N.C_6H_5$$
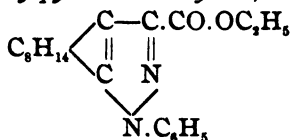
is formed by heating the phenylhydrazide at 200°, or by treating
it with acetic anhydride, glacial acetic acid, or hydrogen chloride.
It crystallizes in bunches of white needles, melts at 114°, and
gives a pale yellow-colored solution with concentrated nitric acid.
The free *acid*, prepared by hydrolyzing the preceding compound,
crystallizes in lustrous needles, which melt at 192°; these appear
to contain benzene of crystallization, as they slowly lose their
luster, even at the ordinary temperature, and then melt at 197°.
The compound, in the form of *sodium salt*, is without marked
physiological action. When the *barium salt* is distilled with
excess of barium oxide, care being taken to avoid the presence of
moisture, an oily compound is formed which gives a reddish
purple coloration with concentrated nitric acid, and also Knorr's
pyrazoline reaction ; it therefore, presumably, contains *camphyl-
phenylpyrazole,*

$$C_8H_{14} \diagup \begin{matrix} C.CH \\ \| \quad \| \\ C \quad N \end{matrix} \diagdown$$
$$\diagdown\diagup$$
$$N.C_6H_5$$
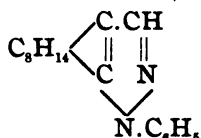
The study of the preceding condensation compounds shows that
their stability increases as the mass of the radical in the amine
becomes greater, at least as regards the aliphatic derivatives ; in
the case of ammonia the symmetry of the molecule probably
accounts for the high melting-point of the product. The ques-
tion as to the formation of compounds of the type,

$$C_8H_{14} \diagup \begin{matrix} C : C.CO.OC_2H_5 \\ | \quad | \\ CO \quad NH.R \end{matrix} \quad \text{or} \quad C_8H_{14} \diagup \begin{matrix} C : C.CONH.R \\ | \quad | \\ CO \quad NH.R \end{matrix} ,$$
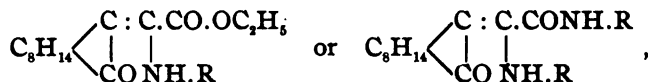
appears to depend upon the basicity of the amine, and the
temperature at which the reaction proceeds ; thus at 100°, when
$R = H$, CH_3, or C_2H_5, compounds of the second type are obtained,
but when $R = NH.NH.CO.NH_2, C_6H_5, NH, C_6H_5$, or $C_{10}H_7$, the
products belong to the first type. At higher temperatures, with
$R = C_6H_5$, a compound of the second type is produced, but under

similar conditions, when $R = C_{10}H_7$, this was not found to be the case. The substances of the first type are strict analogues of the primary condensation products of camphoroxalic acid and amines.

It is worthy of note, that in spite of many attempts to prepare them, no compounds could be isolated in which the carbonyl group of the camphor nucleus had primarily reacted with an amine ; that it had remained intact was proved by the subsequent formation, from the actual condensation-products of pyrazole, and isoxazole derivatives. It is now generally recognized that many α-β, α-γ, and α-Δ-diketones are capable of existing or reacting in two or more forms, the change may be expressed by the equation : $CHR.CO \rightleftharpoons CR:C.OH$. Analogy leads to the conclusion that all compounds of these classes are capable, under suitable conditions of undergoing the change: It is customary to assume that the ordinary "ketonic reagents" react primarily with the carbonyl group, giving compounds of the type of aldehyde ammmonia

$$CHR.C\!\!\begin{array}{c} \diagup NH_2 \\ \diagdown OH \end{array}\!\!,$$
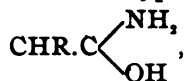
which are generally unstable and change spontaneously into $CHR.C:NH(R)+H_2O$ (formation of oximes, hydrazones, etc.). This idea of the carbonyl group, *always* being the point of attack, does not appear to have any very definite foundation. The above results show that "ketonic reagents," in the presence of a compound containing both carbonyl and the group $R_2C:C.OHR$, react preferably with the latter, and not at all with the former under any conditions hitherto devised, and that, in the case of hydroxylamine, the compound formed by its addition to the double carbon linkage is quite stable. Similar results were subsequently obtained with mesityl oxide and phorone by Harries and his coworkers.[1] The relative stability of such additive compounds would naturally be expected to vary between limits at least as wide as those limiting the existence of the ketonic and enolic forms of the parent substances. Moreover, the stability might be greatly dependent on the reagents with which the compounds are brought into contact. In cases where the group in question could occur twice or thrice, as in triketones, such as

$$R.CO.CH_2.CO.CH_2.CO.R',$$

[1] Ber. d. chem. Ges., 30, 231, 2726 (1897).

the forms,

$$R.COH:CH.CO.CH_2.CO.R'$$

and

$$R.COH:CH.COH:CH.CO.R,$$

might be produced successively as any given reaction proceeded, the end products being, of course, direct derivatives of these forms and not the free enolic bodies themselves. On the other hand, the production of the enolic form might, at any given stage of the reaction, be entirely inhibited by the chemical or stereo-metrical influence of the new groups which become linked to the original molecule. In the preceding sentences, the ketonic and enolic forms of ketones have been referred to, for the sake of simplicity, as if they were fixed quantities; in reality we should doubtless regard them as extreme phases of reversible systems, tending, with very varying velocities, towards more or less widely separated states of equilibrium. The question naturally arises whether the above considerations are not also applicable to monoketones; in this connection, Freer's very interesting researches on acetone may be mentioned; they show that under certain conditions it forms derivatives of the compound $CH_3.COH:CH_2$. An attempt has been made to discover whether any simple relationship exists which would explain the production of highly colored ferric compounds by the enolic forms of diketones and of phenols, but so far, unsuccessfully.

Whatever may be the fate of these suggestions, some explanation must ultimately be given of the following facts: (1) The great reactivity of the "carbonyl" group in camphor with a number of reagents which are generally regarded as tests for the presence of this radical; (2) of the complete quiescence of this group in camphoroxalic acid towards the same reagents; (3) of the great reactivity of the second "carbonyl" in that acid; (4) of the fact that this last group certainly reacts as an unsaturated hydroxyl complex towards some of the reagents, and possibly does so with them all.

Condensation products could not be obtained from ethyl camphoroxalate or sodium camphoroxalate, with the amines enumerated below, under the conditions employed in the preparation of the compounds described in the preceding pages. For convenience both classes of failures are discussed together. *Urea, para-* and *meta-phenylenediamine, ethylaniline,* and *dimethylaniline*

failed to react with either ethyl or sodium camphoroxalate;
α-naphthylamine reacted with the latter but not with the former ;
dimethylamine was only tried with the ethyl salt, with which it
did not combine.   The failure in the case of urea is probably
due to its comparatively feeble basicity, while that with meta-
and para-phenylenediamine is ascribable to the difficulty of pro-
ducing rings of seven and eight members, such as

$$C_8H_{14} \left< \begin{array}{l} C:C\text{------}C.OH \\ |\ \ |\ \ \ \ \ \ \ \ \| \\ CONH\ \ \ \ N \\ |\ \ \ \ \ \ \ \ \ \ | \\ C.CH.C \\ |\ \ \ \ \ \ \ \ \ | \\ HC.CH.CH \end{array} \right.$$

and

$$C_8H_{14} \left< \begin{array}{l} C:C\text{------}C.OH \\ |\ \ |\ \ \ \ \ \ \ \ \| \\ CONH\ \ \ \ N \\ |\ \ \ \ \ \ \ \ \ \ | \\ C.CH.CH.C \\ \llcorner CH.CH.\lrcorner \end{array} \right.$$
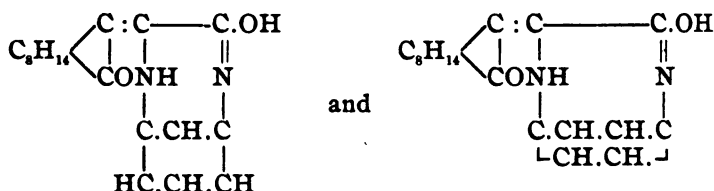
The behavior of secondary amines (ethylaniline and dimethyl-
amine) has already been discussed (cf. p. 372), and dimethyl-
aniline, being a tertiary base, would not be expected to react.
For the failure of α-naphthylamine to condense with ethyl cam-
phoroxalate, while it interacts so readily with sodium camphor-
oxalate, no very plausible reason can, at present, be suggested.

   Ethyl camphoroxalate readily combines with methyl iodide,
in the presence of silver oxide, forming *ethyl methylcamphor-
oxalate* which appears to be an oil ; the corresponding *acid*
crystallizes in six-sided prisms and plates, and melts at 95°–96°.
Like the ethyl salt it gives no coloration with ferric chloride
and alcohol.

   Methyl oxalate condenses with camphor, in presence of
sodium methoxide, but the time of heating requires to be pro-
longed owing to the sparing solubility of the resulting sodium
salt in light petroleum.   It is, therefore, more readily prepared
by esterifying the acid.   The *compound* crystallizes from light
petroleum in arborescent needles, belonging to the orthorhombic
system, which melt at 74.5°–75°.   With phenylhydrazine,
methyl camphoroxalate yields a *phenylhydrazide*, which is
deposited from methyl alcohol in slender, white needles, melting
at 204°–205°.   *Methyl camphylphenylpyrazolecarboxylate*,

$$C_8H_{14} \left< \begin{array}{l} C\text{---}C.CO.OCH_3 \\ \|\ \ \ \ \| \\ C\ \ \ \ N \\ \diagdown \diagup \\ N.C_6H_5 \end{array} \right.$$
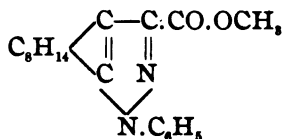
is formed by the interaction of the phenylhydrazide and glacial acetic acid. It crystallizes in colorless needles, melts at 80.5°–81.5°, and when hydrolyzed yields the acid (m. p. 193°–194°) described above (p. 381).

The preparation of *isoamyl camphoroxalate* was necessarily preceded by that of isoamyl oxalate. The only method described in Beilstein's "Handbuch" is due to Friedel and Crafts, and consists in heating ethyl oxalate with isoamyl alcohol at 220°–250°. No difficulty was experienced in obtaining the compound, in any desired quantity, by the action of isoamyl alcohol on dehydrated oxalic acid at 100°. The preparation of *isoamyl camphoroxalate* was carried out in a similar manner to that of the ethyl salt. The sodium dissolves easily, and the resulting compound is readily soluble in light petroleum. The isoamyl salt itself is sparingly soluble in ether, and crystallizes in colorless triclinic needles, melting at 98.5°–99.5°. The chief object in view in preparing this compound was to ascertain the influence, if any, of the increase of the mass of the carbalkyloxy group on the course of the condensation. The results show that it proceeds more readily with the higher than with the lower homologues ; the solubility in ether or light petroleum of ethereal sodium salts also increases as the mass of the alkyl becomes greater, and it is highly probable that this is the chief reason, if not practically the only one, for the improved yield, as the sodium is more readily dissolved. On the other hand the solubility of the free ethereal salts in ether and light petroleum is least in the case of isoamyl, greatest in that of ethyl, while methyl occupies the intermediate position. As regards melting-points the compounds resemble the corresponding ethereal salts of oxalic acid since the ethyl derivative melts at a lower temperature than the methyl salt.

Isoamylic camphoroxalate phenylhydrazide, prepared in a similar manner to the lower homologues, is very sparingly soluble in ordinary media, with the exception of isoamyl alcohol, at the boiling-point of which it slowly suffers decomposition.

Condensation takes place tolerably readily between camphor and ethyl pyruvate ; the product is difficult to purify and has, therefore, hitherto not been investigated.

EXPERIMENTAL.

Camphoroxalic Acid.

The best method of preparing this compound in quantity has been previously described.[1]

Ammonia and Camphoroxalic Acid.

The acid (4.4 grams = 1 mol.) was mixed in a bottle of about 150 cc. capacity, with ammonium chloride (3.2 grams = 3 mol.), potassium hydroxide (4.5 grams = 4 mol.) and alcohol (95 per cent., 50 cc.) ; the bottle was provided with a well fitting glass stopper which was suitably clamped, and the contents heated at 100° in a water-bath during four hours.   When cold, the alcohol was removed by evaporation, and the residue treated with water, acidified with dilute sulphuric acid, and extracted three times with ether.   The solid residue from the dried ethereal solution was then recrystallized several times from benzene, and finally from a mixture of acetone and light petroleum.   The compound, which is *camphorformeneamine carboxylic acid*, is deposited in colorless plates melting at 178° with evolution of gas ; it is readily soluble in benzene, acetone, and ethyl acetate, insoluble in light petroleum.   It does not dissolve in sodium carbonate solution at the ordinary temperature, but does so readily when heated, and is reprecipitated on acidification.   With alcohol and ferric chloride no coloration is produced, but a deep red one is obtained if the compound is previously treated with hydrochloric acid and potassium nitrite.   Sodium hydroxide may be employed for the preparation of the compound instead of potassium hydroxide.

Analysis :

I. 0.2485 gram substance gave 0.5850 gram carbon dioxide and 0.1720 gram water.

II. 0.1946 gram substance gave 10 cc. nitrogen at 13° and 755 mm.

III. 0.1207 gram substance gave 6.8 cc. nitrogen at 28.5° and 741.5 mm.

	Calculated for $C_8H_{14}\Big\langle\begin{smallmatrix}C : C.CO.OH\\ CONH_2\end{smallmatrix}$	Found.		
		I.	II.	III.
Carbon..........	64.57	64.20	....	....
Hydrogen	7.62	7.69	....	....
Nitrogen	6.28	....	6.04	6.01

When heated at 170°–180°, the compound evolves gas ; the resinous residue dissolves in alcohol, and also in hydrochloric

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[1] *Am. Chem. J.*, **19**, 399 (1897) ; **21**, 247 (1899).

acid; from this latter solution sodium hydroxide precipitates an amorphous substance, while platinic chloride gives crystals of ammonium platinichloride, which were identified by analysis and comparison with a pure preparation of that salt.   It is thus evident that the attempt to eliminate the carboxyl group in this simple manner from the original compound was unsuccessful.

By the action of free camphoroxalic acid on absolute alcoholic ammonia, in excess, at 100°, under pressure, a crystalline compound is formed which melts and evolves gas at about 212°, but when very slowly heated it melts at about 100°.   Ammonia is evolved when the compound is boiled with aqueous sodium hydroxide, and the solution, after acidification, gives a deep red coloration with ferric chloride and alcohol.   The compound is presumably *ammonium camphoroxalate*.

ETHYL CAMPHOROXALATE DERIVATIVES.

Ammonia and Ethyl Camphoroxalate.—The ester (5 grams = 1 mol.) was mixed with ammonium chloride (3.2 grams = 3 mol.), potassium hydroxide (3.1 grams = less than 3 mol.), and alcohol of 95 per cent. (50 cc.).   The mixture was then heated in a closed bottle, at 100°, during four hours.   The alcohol was removed on the water-bath, the residue washed with water and dried.   The yield is practically quantitative.   The compound is sparingly soluble in chloroform, acetic acid, alcohol, and benzene, but readily in xylene ; it was crystallized from this three times, and after being washed with benzene formed colorless, microscopic needles melting at 227°-228°.

Analysis :

I. 0.2158 gram substance gave 0.5086 gram carbon dioxide.
II. 0.2135 gram substance gave 0.5040 gram carbon dioxide and 0.1560 water
III. 0.1274 gram substance gave 14.0 cc. nitrogen at 18.5° and 743 mm.
IV. 0.1323 gram substance gave 15.4 cc. nitrogen at 19.5° and 747 mm.
V. 0.2061 gram substance gave 23.4 cc. nitrogen at 17.5° and 750 mm.

	Calculated for $C_8H_{14}\begin{cases}C:C.CONH_2\\CONH_2\end{cases}$	Found.				
		I.	II.	III.	IV.	V.
Carbon......	64.86	64.28	64.38	....	....	....
Hydrogen ...	8.10	....	8.11	....	....	....
Nitrogen	12.61	....	....	12.31	13.11	12.97

Camphoformeneaminecarboxylamide gives no coloration with ferric chloride and alcohol ; when boiled with aqueous sodium

hydroxide, ammonia is evolved, and the residue, after acidifying, gives, on the addition of ferric chloride and alcohol, the deep red coloration characteristic of camphoroxalic acid. The amide is also produced by heating ethyl camphoroxalate, or the ammonia additive compound of this mentioned below, with alcoholic ammonia at 100° in a sealed tube ; the yield is excellent, but the method is not so convenient as the one given above. With alcoholic hydroplatinichloric acid the amide yields a sparingly soluble *platinichloride* which crystallizes in hexagonal, orange-colored plates.

A second compound of ammonia and ethylic camphoroxalate is obtained by saturating a concentrated, well cooled solution of the latter, in absolute alcohol or ether, with the anhydrous gas. A white precipitate is formed, which, when removed, and drained on a porous plate, is gradually resolved into its constitutents. The substance could not be analyzed, but is almost certainly the simple additive *compound*

$$C_8H_{14}\left\langle\begin{array}{l}CH.COH.CO.OC_2H_6\\ | \quad |\\ CO \ NH_2\end{array}\right.$$
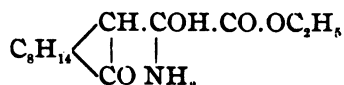
When heated with alcoholic ammonia in a sealed tube at 100°, camphoformeneaminecarboxylamide is obtained as described above. A third *compound*, which has been previously described, was obtained by the action of dried ammonia on *crude* ethylic camphoroxalate in anhydrous ethereal solution; it darkens at about 200°, melts at 225°, and is possibly impure oxamide, as subsequent experiments with the purified ester failed to yield it.

Hydroxylamine and Ethyl Camphoroxalate.

The ester (1 mol.) is dissolved in alcohol and mixed with a concentrated, aqueous solution of hydroxylamine hydrochloride (3.5 mol.); more alcohol is added if necessary to obtain a clear solution, and then solid sodium hydrogen carbonate until the liquid is slightly alkaline. The mixture is allowed to remain at the ordinary temperature during six days, in the course of which a white granular precipitate gradually forms. The liquid is then poured into water, acidified with dilute sulphuric acid, and extracted three times with ether. The ethereal solution is dried and distilled, and the residue crystallized twice from a mixture of toluene and light petroleum ; it is deposited in colorless, slender needles melting at 120°–121°. The *compound* is readily soluble

in aqueous sodium hydroxide, more slowly in sodium carbonate solution ; it dissolves in dilute sulphuric acid when heated, but crystallizes out on cooling. It does not appear to be soluble in water to any great extent, but when heated it melts and floats on the surface. An attempt to obtain the compound by the inter-action of its constituents at 100°, under pressure, in the manner described in the preparation of camphoformeneaminecarboxyl-amide was not successful, neither did the ester react at all with hydroxylamine in absolute alcoholic solution, under pressure, at 100°. The constitution of this substance will be further investi-gated subsequently.

In the first paper on this subject (*loc. cit.*) brief mention was made of a *compound* obtained from *crude* ethylic camphoroxalate and hydroxylamine, as the latter was employed in the form of hydrochloride, and a large excess of potassium hydroxide added; it follows that the substance should be a derivative of a cam-phoroxalic acid and not of the ethyl salt. The body has now been further investigated, and it appears to be a *potassium salt* of an oxalic acid derivative ; this is readily understood when it is remembered that the only specimens of ethyl camphoroxalate at that time procurable necessarily contained ethyl oxalate in vary-ing proportion. The compound crystallizes in colorless, silky needles, melts at 193° with sudden decomposition, is readily solu-ble in water and sodium hydroxide solution, more sparingly in dilute alcohol, and is practically insoluble in absolute alcohol. It gives a red coloration with alcohol and ferric chloride after being boiled with hydrochloric acid, but oxalic acid could not be detected in the solution. The readiness with which it explodes, on heating, rendered the analysis so difficult that, after several unsuccessful attempts, further effort was abandoned.

Methylamine and Ethyl Camphoroxalate.—The ester (5 grams = 1 mol.) was mixed with methylamine hydrochloride (4 grams = 3 mol.), potassium hydroxide (3 grams = less than 3 mol.) and alcohol (95 per cent., 50 cc.) and heated under pressure, at 100°, during four hours. The alcohol was removed on the water-bath, the residue treated with water, and extracted with ether. The ethereal solution, after drying, was distilled. The crystal-line residue consisted of *methyl camphoformeneaminecarboxyl-methylamide;* it was purified by repeated crystallization from benzene, with the addition of light petroleum, and was deposited

in small, white needles, melting at 130°. The compound is less readily soluble in benzene than the ethyl derivative described below, and is somewhat unstable ; on this account, and from the difficulty of completely freeing it from ash, which contained iron, its analysis was abandoned after several unsuccessful attempts had been made.

The aqueous liquid remaining after the removal of the amine was acidified with dilute sulphuric acid, and extracted with ether; this, after drying and distillation, gave only a small residue consisting, apparently, of impure camphoroxalic acid.

Ethylamine and Ethyl Camphoroxalate.—The experiments with ethylamine were carried out exactly as in the case of methylamine, the quantities of materials employed being ester (5 grams = 1 mol.), ethylamine hydrochloride (3.2 grams = 2 mol.), potassium hydroxide (2 grams = less than 2 mol.), and 95 per cent. alcohol, (50 cc.). The product, *ethyl camphoformeneaminecarboxylethylamide*, readily dissolves in ethyl acetate and benzene, but is insoluble in light petroleum. It gives no coloration with alcohol and ferric chloride solution, but even when purified, slowly evolves ethylamine. It is deposited from benzene, after two crystallizations, in colorless needles melting at 148°. The yield is good. The compound is also formed by the action of free ethylamine on the ester, in absolute-alcoholic solution at 100°, under pressure.

Analysis :

I. 0.2606 gram substance gave 0.6558 gram carbon dioxide and 0.2262 gram water.

II. 0.1326 gram substance gave 11.8 cc. nitrogen at 18.5° and 739 mm.

	Calculated for $C_8H_{14} \begin{cases} C:C.CONH.C_2H_5 \\ | \quad | \\ CONH.C_2H_5 \end{cases}$	Found.	
		I.	II.
Carbon	69.06	68.63	..
Hydrogen	9.35	9.64	..
Nitrogen	10.07	..	9.96

Ethyl Camphoroxalate and Methyl Iodide.—The ethyl salt (2.5 grams) was mixed with dried silver oxide (3.5 grams),[1] and methyl iodide (3 grams), and heated in a sealed tube, at 100°, during four hours. The product was filtered, the silver compounds repeatedly washed with ether, and the combined filtrate and washings allowed to evaporate. The residue did not crystallize. It consisted of *ethyl methylcamphoroxalate* as it gave

[1] Cf. Lauder : *J. Chem. Soc.* (London), **77**, 729 (1900).

no coloration with alcohol and ferric chloride. The correspond-
ing *acid*,

$$C_8H_{14}\left\langle\begin{array}{l}C : C(OCH_3).CO.OH\\|\\CO\end{array}\right.$$
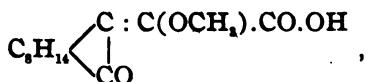
was obtained by hydrolyzing the preceding compound with dilute
aqueous-alcoholic sodium hydroxide at 100°. It readily crystal-
lizes from light petroleum in large hexagonal-shaped prisms and
plates, and melts at 95°–96°. It gives no coloration with alcohol
and ferric chloride, but with ammonium hydroxide and calcium
chloride it gives a white precipitate soluble in acetic acid, thus
resembling camphoroxalic acid. It is apparently gradually con-
verted into this acid on exposure to the air.

Ethyl Camphoroxalate and Acetone.—These two compounds do
not appear to react when mixed and treated with sodium in equi-
molecular proportion, in the presence of light petroleum. Some
of the metal immediately dissolves, but the remainder is not
attacked after boiling during two hours. Sufficient absolute
alcohol was added to combine with the sodium, but the only
product which could be eventually isolated was camphoroxalic
acid. The similar negative result was obtained with *ethyl
camphoroxalate and camphor*, the experiments being carried out
under similar conditions to those just described.

Ethyl Pyruvate.—This compound can be readily prepared by
the method of esterfication previously described (*loc. cit.*). Pyruvic
acid (50 grams) is mixed with 95 per cent. alcohol (500 cc.), and
conc. sulphuric acid (80 cc.) and boiled during seven hours. The
excess of alcohol is removed on the water-bath, the acid being
simultaneously neutralized with sodium hydrogen carbonate, the
product poured into water, extracted with ether, and the ethereal
solution washed, if needful, with sodium hydrogen carbonate
solution.

Ethyl Pyruvate and Camphor.—When treated with camphor,
(1 mol.) and sodium wire (1.5 atoms), in light petroleum solution,
condensation apparently takes place. The product has hitherto
proved difficult to purify; it gives a deep red coloration with ferric
chloride and alcohol.

The work will be continued and extended in various directions
as time permits.

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SYNTHESIS OF DERIVATIVES OF DIMETHYLCYCLOPEN-TANONE, ββ-DIMETHYLADIPIC ACID, AND αββ-TRI-METHYLADIPIC ACID.[1]

BY W. A. NOYES.

SOME time since, the author reported on the synthesis of 2.33-trimethylcyclopentanone,[2] and its identification with a ketone previously obtained from camphoric acid by a series of easily interpreted reactions. As the study of this ketone and of related compounds, seems likely to prove of some importance in the further development of the chemistry of camphor and of the terpenes, it appears desirable to give in greater detail the methods used in their preparation.

The investigation of some of the derivatives of cyclopentanone involved has also led to the discovery that some of them decompose in a manner which is, so far as I am aware, quite new.

Phosphorus Tribromide.—Fifty grams of yellow phosphorus were dissolved in 100 grams of carbon disulphide in a flask, the lip of which had been cut off. The flask was connected with an upright condenser by means of a piece of rubber tubing slipped over both. A little more than the theoretical amount of bromine (about 125 cc.) was measured into a drop-funnel which was then hung in the top of the condenser. The bromine was then allowed to drop as rapidly as possible without the escape of carbon disulphide or bromine vapors. The carbon disulphide boils from the heat of the reaction and, condensing above, dilutes the bromine as it flows down. The whole of the bromine may usually be added in forty to fifty minutes. The completion of the change of the phosphorus to the tribromide, is indicated sharply by a change from yellow to a reddish color. The solution is then distilled from a Ladenburg bulb till a temperature of 165° is reached. The residue is sufficiently pure for use. A small additional amount may be obtained by distilling, in the same manner, the portion which passes over, and the yield is then almost quantitative.
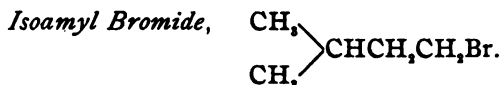
Isoamyl Bromide, $\begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!CHCH_2CH_2Br.$

480 grams of fusel oil (boiling-point 128°–132° and consisting mainly of methyl-3-butanol,

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \Big\rangle CHCH_2CH_2OH)$$

were put in a flask and 437 grams of the phosphorus tribromide were added in portions, with constant cooling, the whole being added within half an hour. The mixture was allowed to stand over night and was then warmed for a couple of hours on the water-bath, a little water being added from time to time to prevent much evolution of hydrobromic acid. The evolution of hydrobromic acid indicates that the reaction takes place in part with the formation of esters of phosphorous acid, but the hydrobromic acid formed may, if retained, still react with the esters or with amyl alcohol. The mixture separated into two layers. The lower layer was separated and distilled slowly, with the addition of some pieces of porous tile to prevent bumping, till a temperature of 140° was reached by a thermometer in the liquid.

The distillate was mixed with the portion of isoamyl bromide previously separated, and the whole shaken twice with sulphuric acid which had been diluted with an equal volume of water, to remove hydrobromic acid, twice with concentrated sulphuric acid, to remove amyl alcohol, then with water and with a solution of sodium carbonate, and finally with dry sodium sulphate to dry and clear it. After filtering, it is sufficiently pure for the present use. Yield, 636 grams, or 88 per cent. of the theory.

Isocaproic Acid,

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \Big\rangle CHCH_2CH_2CO_2H$$

(methyl-4-pentanoic acid).—The only method of preparing iso-amyl cyanide given by Beilstein, is from isoamyl chloride. The use of the bromide gives, in my experience, at least, very much better yields. For the preparation of isocaproic acid, the separation of the cyanide is not necessary. 280 grams of potassium cyanide were dissolved in 300 cc. of hot water, 1250 cc. of alcohol, and 636 grams of amyl bromide were added, and the whole boiled on a water-bath in a flask connected with an upright condenser for twenty-four hours. The solution was then poured from the potassium bromide, which separated, into a second flask

containing 350 grams of caustic potash, and the boiling continued for twenty-four hours longer. The solution was transferred to a large porcelain dish and evaporated with the addition of water, till the alcohol was removed. The residue was transferred to a flask containing 400 cc. of dilute sulphuric acid (1:1 by volume), and the isocaproic acid, which separated, was distilled. The acid solution was extracted once with ligroin. The yield was 401 grams, or 82 per cent. of the theory.

The method here given for the preparation of isocaproic acid may be used with advantage in the preparation of other acids and especially in the preparation of propionic acid, but requires some modification in details.

Isocaprolactone,

$$\begin{array}{l} CH_3 \\ \diagdown \\ \diagup C-CH_2CH_2CO \\ CH_3 | | \\ O\text{------------}| \end{array}$$
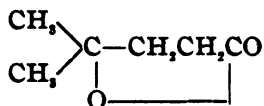
(4-methyl-1.4-pentanolide).—300 grams of isocaproic acid and 150 grams of sodium hydroxide were dissolved in 900 cc. of water, the solution was cooled, and 4.5 liters of a 10 per cent. slightly warm solution of potassium permanganate were added in portions of 500 cc. at a time, at intervals of one-half hour to one hour. Considerable heat is produced by the reaction and external heating is not necessary. A temperature of 50°–60° seems to be most desirable. The final decolorization of the permanganate may be hastened by warming on the water-bath. The filtrate and washings from the oxides of manganese were concentrated to about 600 cc. and poured into 350 cc. of dilute sulphuric acid (1:1 by volume). The mixture of isocaproic acid and lactone was separated from the acid solution and the latter was distilled with steam till about a liter had passed over. The mixture of acid and lactone was shaken with the distillate in portions of 300 cc. at a time, separating the aqueous solution each time, and then with water in the same manner till 4 or 5 liters have been used. By this treatment the lactone gradually passes into the aqueous solution, while most of the unchanged isocaproic acid remains behind. If an emulsion forms, a little ligroin can be added to clear the solution and does not seem to interfere with the extraction of the lactone by the water.

If desired, the amounts of acid and lactone in the successive

aqueous extracts can be followed approximately by titrating with tenth-normal caustic potash, with phenolphthalein as an indicator. The direct titration of the cold solution gives the amount of acid; then on adding an excess of the alkali, warming in a covered flask on the water-bath for a few minutes, and titrating back with tenth-normal acid, the difference between the excess of alkali added and the acid used, corresponds to the amount of lactone present.

The residual isocaproic acid is distilled to a temperature of 190° to remove the ligroin, and may then be used for a new oxidation.

The aqueous solution is then made strongly alkaline with sodium hydroxide, making sure enough is present to combine with all of the lactone, and warming the solution at first in a flask to avoid loss. It is then evaporated to a volume of 200 cc. or less, poured into dilute sulphuric acid, the mixture of acid and lactone separated, and the solution extracted several times with ether.

The mixture of lactone and acid is then exactly neutralized with a 30 per cent. solution of potassium hydroxide, added in portions, the mixture being shaken and cooled quickly after each addition. Fifteen to 20 grams of dry potassium carbonate are added and the solution is extracted repeatedly with ether. After extraction the alkaline solution is acidified, the isocaproic acid, which separates, is added to the mixture of lactone and acid obtained by a new oxidation, and the aqueous solution is also distilled with steam to recover some of the lactone which it retains.

The ethereal solutions are dried with a little sodium sulphate and distilled. If enough potassium carbonate was used to remove all of the isocaproic acid a pure lactone is obtained by one distillation. The boiling-point is 208°–208°.5 and the melting-point 10°. Bredt and Fittig give the boiling-point as 207°[1] and melting-point as 7°–8°.[2] The yield is 35 to 40 per cent. of the portion of the isocaproic acid oxidized. Bredt and Fittig obtained a yield of 25 to 30 per cent.

γ-*Chloroisocaproic Ester*,[3]

$$CH_3\!\!>\!\!CClCH_2CH_2CO_2C_2H_5.$$
$$CH_3$$

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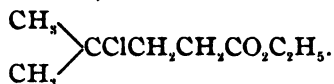
[1] *Ann. Chem* (Liebig), **208**, 55.

[2] *Ibid.*, **200**, 260.

[3] Bredt : *Ber. d. chem. Ges.*, **19**, 514.

In the original synthesis of trimethylcyclopentanone the
γ-bromisocaproic ester was used. It has been found that better
yields are obtained by the use of the corresponding chlorine
derivative. Fifty grams of the lactone were mixed with 150 cc.
of absolute alcohol and the solution in a bottle, surrounded with
cold water, was saturated with hydrochloric acid gas, from 90
to 100 grams being required. After standing over night the
solution was poured on crushed ice, the ester, which separated,
washed two or three times with a little salt water, dried with
sodium sulphate and filtered. The aqueous solution was
extracted two or three times with low boiling ligroin, the ligroin
being distilled away under diminished pressure. The yield is 71
to 73 grams, or 90 to 93 per cent. of the theory.

Dimethylcyancarboxethylcyclopentanone,
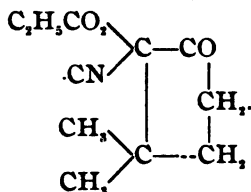
The preparation[1] of this substance and proof of its structure[2] have
been given. In its further preparation, 250 grams of bromiso-
caproic ester gave 25 grams of the pure, crystallized substance.
Better yields could probably be obtained by the use of the chlor-
isocaproic ester, but this has not been tried.

When the substance is boiled with dilute hydrochloric acid, it
decomposes very slowly with evolution of carbon dioxide. In
sealed tubes, at 150°–160°, the decomposition is more rapid, but
still requires two or three hours. The products of decomposition
are *acetic acid, isocaprolactone,* and *carbon dioxide.* The lactone
boiled at 206°–209° and was analyzed, giving 62.83 per cent. of
carbon and 8.62 per cent. of hydrogen. Theory requires 63.16
and 8.77 per cent. The silver salt gave 44.92 per cent. silver.
Theory requires 45.19 per cent.

When saponified with alcoholic potash, *malonic acid,* melting
at 133°, and *isocaprolactone,* boiling at 208°–209° and melting at
10°, were obtained.

The decomposition here described is, of course, related to the

---

[1] *Am. Chem. J.*, 22, 259.
[2] *Ibid.*, 23, 135.

"acid decomposition" of acetacetic ester and its derivatives, but I do not recall any other case in which a carbon atom is removed from a ring and replaced by oxygen in this manner. A similar case will, however, be described further on, and the decomposition will, undoubtedly, be found typical for bodies of similar structure.

So far as the purpose of the experiments in working toward a synthesis of camphoric acid is concerned, the result was, of course, disappointing. At the end of a considerable amount of work, the original lactone was obtained instead of the dimethyl-carboxethylcyclopentanone, which had been sought.

3,3-Dimethyl 2,2-dicarboxethyl cyclopentanone,

$$\begin{array}{l} C_2H_5CO_2 \\ \qquad\qquad\diagdown \\ \qquad\qquad\qquad C\!\!-\!\!CO \\ C_2H_5CO_2\diagup \quad |\qquad | \\ \qquad\qquad\qquad\quad CH_2. \\ \quad CH_3\diagdown\ |\qquad | \\ \qquad\qquad\qquad C\!\!-\!\!CH_2 \\ \quad CH_3\diagup \end{array}$$
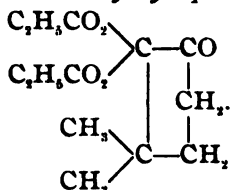
115 grams of sodium were dissolved in 130 cc. of absolute alcohol, 85 grams of *pure*[1] malonic ester were added and 89 grams of the γ-chloroisocaproic ester. The mixture was heated on the water-bath from four to six hours; most of the alcohol was then distilled by heating on the water-bath under diminished pressure. The residue was cooled, water added, and the oil which separated was dried with sodium sulphate and fractioned under diminished pressure, the lower boiling portions being distilled twice. The aqueous solution was also extracted once or twice with ether.

The portion boiling below 80° under a pressure of 20 mm., consists mainly of pyroterebinic ester,

$$\begin{array}{l} CH_3\diagdown \\ \qquad\quad C\!=\!CHCH_2CO_2C_2H_5, \\ CH_3\diagup \end{array}$$

that from 90° to 100° of malonic ester with some chlorisocaproic ester, and that from 170°–180° of the dimethyldicarboxethyl-cyclopentanone. The yield of the last compound was about 20 per cent of the weight of the chlorisocaproic ester used.

[1] When malonic ester is prepared by the method described in this Journal, **18**, 1105 (1896), it contains considerable amounts of cyanacetic ester, and the conversion to malonic ester is not complete after many hours' heating of the acid-alcoholic solution. The ester prepared by Claissen's method, *Ann. Chem.* (Liebig), **218**, 131, would probably contain some of the same impurity. For the present purpose a pure ester prepared from calcium malonate is required.

The pyroterebinic ester may be saponified with alcoholic potash, the pyroterebinic acid converted into isocaprolactone by boiling for a short time with dilute sulphuric acid (1 : 1 by volume) and the latter purified by treatment with potassium hydroxide and potassium carbonate as before. The recovered malonic ester may, of course, be used repeatedly.

Dimethyldicarboxethylcyclopentanone is a nearly colorless oil which boils at 167°–169° under a pressure of 14 mm.

0.1831 gram gave 0.1328 gram water and 0.4086 gram carbon dioxide.
0.2208 gram gave 0.1594 gram water and 0.4892 gram carbon dioxide.

	Calculated for $C_{12}H_{20}O_5$.	Found.	
		I.	II.
Carbon	60.94	60.83	60.43
Hydrogen	7.77	8.06	8.02

When dimethyldicarboxethylcyclopentanone is saponified by warming with an excess of alcoholic potash or soda, it breaks down in the same manner as dimethylcyancarboxethyl-cyclopentanone (p. 396), giving malonic and hydroxy iso-caproic acids. In some cases, by careful saponification in a cold solution, there was obtained a small amount of the tribasic acid

$$
\begin{array}{c}
CH_3 \\
\diagdown \\
CH_3 \diagup C-CH \diagup \begin{array}{c} CO_2H \\ \\ CO_2H \end{array} \\
| \\
CH_2-CH_2CO_2H,
\end{array}
$$
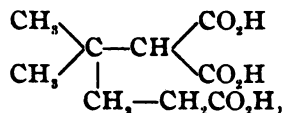
and at one time it was thought that this acid was formed by the saponification of the cyclic compound. A further study of the matter, however, makes it very probable that the tribasic acid was formed chiefly, if not altogether, from a small amount of the ester of that acid which had failed to condense to the cyclic compound. In one case, a considerable amount of dimethyladipic acid was found among the products of the saponification. This indicates that the cyclic compound had, in part, undergone the ketonic decomposition, giving the compound

$$
\begin{array}{c}
CH_3 \\
\diagdown \\
CH_3 \diagup C-\!\!-\!\!-CH-CO_2C_2H_5 \\
| | \\
| CO \\
| | \\
CH_2-CH_2
\end{array}
$$
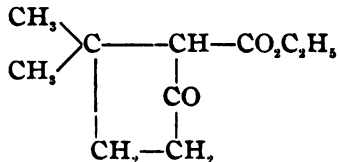
This would then saponify to $\beta\beta$-dimethyladipic acid. It is also possible, however, that the ester of the tribasic acid decomposes partly on distillation, forming the ester of dimethyladipic acid.

Triethyl Ester of 3,3-Trimethylhexanoic, 1,2',6 Acid,

$$\begin{array}{c} CH_3 \\ \diagdown C-CH \diagup \begin{array}{c} CO_2C_2H_5 \\ \diagdown CO_2C_2H_5 \end{array} \\ CH_3 \diagup \quad | \quad \diagdown CO_2C_2H_5 \\ \quad CH_2-CH_2-CO_2C_2H_5 \end{array}$$
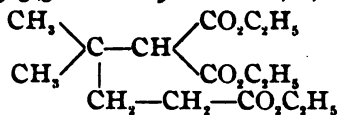
When 8.5 grams of sodium are dissolved in 140 cc. of absolute alcohol and the solution is dropped slowly, during two or three hours, into a mixture of 66 grams of chlorisocaproic ester and 75 grams of pure malonic ester, the ester of the tribasic acid is formed and its condensation to the cyclic ester is largely prevented. After heating for an hour longer, the product was treated as described above under the cyclic compound. Ten grams of the ester boiling at 150°–172°, under a pressure of 15 mm., were obtained. The boiling-point is apparently very nearly the same as that of the dimethyldicarboxethylcyclopentanone. Analysis I, below, was made with the ester prepared as described, and distilled but once. Analysis II was with an ester prepared from the pure crystallized acid by treatment with alcohol and hydrochloric acid as usual.

I. 0.2467 gram gave 0.1865 gram water and 0.5374 gram carbon dioxide.
II. 0.1612 gram gave 0.1276 gram water and 0.3521 gram carbon dioxide.

	Calculated for $C_{15}H_{26}O_6$.	Found.	
		I.	II.
$C_{15} =$	$180 = 59.60$	59.00	59.58
$H_{26} =$	$26 = 8.61$	8.40	8.80
$O_6 =$	$96 = 31.79$		
	$\overline{302}$		

33-*Trimethylhexanoic*-1,2',6 *Acid*, obtained from the ester by saponification, crystallizes from water in compact crystals which melt at 165°–175° with decomposition, the temperature of melting being dependent on the rate of heating. The acid is very difficultly soluble in ether, and rather difficultly soluble in cold water.

0.2791 gram gave 0.1629 gram water and 0.5047 gram carbon dioxide.

	Calculated for $C_9H_{14}O_6$.	Found.
Carbon..............	49.54	49.32
Hydrogen...........	6.42	6.49

The *calcium salt*, $Ca_3(C_9H_{11}O_6)_2 + 5H_2O$, was prepared by dissolving the acid in ammonia, adding calcium chloride and heating the solution on the water-bath. The salt which separated was filtered off, dissolved in cold water and the salt precipitated a second time by warming and evaporating the solution. The salt

is moderately soluble in cold water, and much less soluble in hot water. The portion which separates on warming the solution dissolves on cooling, while the calcium salt of dimethyladipic acid, which separates on warming, does not redissolve on cooling. These facts may be used to advantage in separating mixtures of the two acids.

The salt dried over sulphuric acid lost 13.69 per cent. water. Theory requires for $5H_2O$ 14.06 per cent. The dry salt gave 21.79 per cent. calcium. Theory requires 21.81 per cent.

ββ-Dimethyladipic Acid,

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \hspace{-1.2em} C-CH_2-CO_2H \\ CH_3 \quad | \\ \hspace{1.5em} CH_2CH_2-CO_2H \end{array},$$
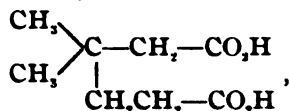
is formed quantitatively, when the acid last mentioned is heated for a short time to 200°. The acid is easily soluble in hot water and in ether, difficultly soluble in cold water, and almost insoluble in ligroin. It crystallizes from water in small plates. It melts at 102°.

0.2052 gram gave 0.1490 gram water and 0.2160 gram carbon dioxide.
0.1934 gram gave 0.1401 gram water and 0.3926 gram carbon dioxide.

	Calculated for $C_8H_{14}O_4$.	Found.	
		I.	II.
Carbon	55.17	55.25	55.36
Hydrogen	8.05	8.07	8.05

0.1136 gram of the acid took 13.13 cc. tenth-normal caustic potash. Theory requires 13.05 cc.

The *calcium salt*, $Ca(C_8H_{12}O_4)+nH_2O$, is most easily prepared by dissolving the acid in ammonia, adding calcium chloride and boiling the solution. No precipitate forms till the solution is warmed. The salt, when once formed, is difficultly soluble but may be crystallized by evaporating its solution, when it is deposited in pearly scales. The salt prepared in this manner lost 21.99 per cent. of water at 140°, while that prepared by precipitation lost only 6.18 per cent. The dried salts gave, respectively, 18.72 and 19.16 per cent. of calcium. Theory requires 18.87 per cent.

The *silver salt* was prepared by adding silver nitrate to a solution of the calcium salt. It is almost entirely insoluble in water. The analysis gave 55.38 per cent. silver. Theory requires 55.67 per cent.

The *copper salt* is precipitated as a green powder on adding copper acetate to an aqueous solution of the acid.

Some time ago Tiemann[1] obtained from ionone an acid which he supposed to be $\beta\beta$-dimethyladipic acid and which melted at 87°. The $\alpha\alpha$-dimethyladipic acid which he describes melts at the same temperature.[2] Baeyer[3] has also obtained a dimethyladipic acid which melts at 87°-88° by the oxidation of tetrahydroeucarvone. He seems to imply that his acid is the $\beta\beta$-acid but does not make a definite statement to that effect. Since $\beta\beta$-dimethyladipic acid contains no asymmetric carbon atom, stereoisomerism is extremely improbable and no evidence of its existence has appeared in my study of the body. It would seem, therefore, that if the acids obtained by Tiemann and Baeyer were pure, they must possess another structure than that ascribed to them.

Triethyl Ester of 2,33- Trimethylhexanoic 1,2',6 Acid,

$$CH_3-C\begin{cases}CO_2C_2H_5\\CO_2C_2H_5\end{cases}$$
$$\begin{matrix}CH_3\\ \\CH_3\end{matrix}\Big\rangle C-CH_2-CH_2-CO_2C_2H_5$$
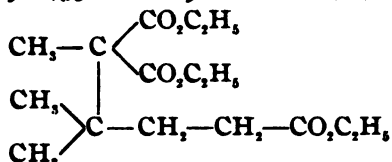
The preparation of this compound by the condensation of γ-brom-isocaproic ester with the diethyl ester of methyl malonic acid has been described.[4] It has been found that to obtain a pure product, the methyl malonic acid must be purified by crystallization from water[5] and so freed from malonic acid, which it will contain if prepared by the condensation of malonic ester with methyl iodide. The yield is improved somewhat by the use of γ-chlorisocaproic ester in place of the bromine derivative but it is always poor. A better method of preparation consists in the condensation of the triethyl ester of the trimethyl hexanoic acid described above (p. 399) with methyl iodide by means of sodium ethylate.

$\alpha\beta\beta$- Trimethyladipic Acid,

$$CH_3-CH-CO_2H$$
$$\begin{matrix}CH_3\\ \\CH_3\end{matrix}\Big\rangle C-CH_2CH_2CO_2H$$
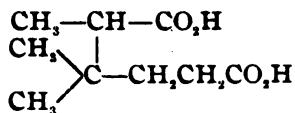
[1] *Ber. d. chem. Ges.*, **31**, 860, 884.
[2] *Ibid.*, **31**, 883.
[3] *Ibid.*, **31**, 2074.
[4] *Am. Chem. J.*, **23**, 128.
[5] Perkin : *J. Chem. Soc.* (London), **45**, 510.

This acid is formed when the 33-trimethylhexanoic-1,2′,6 acid is heated for a short time to 200°. It appears to exist in two forms, a fumaroid and a maleïnoid form. Only the former has thus far been obtained pure. The acid was purified by crystallization from water and from ether. It is difficultly soluble in cold water and in ether, almost insoluble in ligroin. It crystallizes from water or from ether in leaflets which melt at 136°.

o.1637 gram of the acid gave 0.1286 gram water and 0.3424 gram carbon dioxide.

	Calculated for $C_9H_{16}O_4$.	Found.
Carbon	57.44	57.04
Hydrogen.................	8.52	8.73

ROSE POLYTECHNIC INSTITUTE, TERRE
HAUTE, IND., April 25, 1901.

A NEW INDICATOR FOR USE IN DETERMINING TOTAL ACIDITY OF WINES.[1]

BY E. G. RUNYAN.

IN maintaining a chemical control of a beet sugar house, it is often necessary to determine by some rapid method the excess of alkali in the juices, sirups, and massecuites. The usual method is to titrate the material with a standard acid solution. As these products vary in color from a light amber to a dark brown, or nearly black, the ordinary indicators often give very unsatisfactory results, or fail entirely, on account of the difficulty of noting the end reaction.

To meet this difficulty, a French chemist, L. Lachaux, in 1892, proposed a mixture of corallin and malachite green[2] prepared as follows:

Three and one-tenth grams of corallin or commercial rosolic acid are dissolved in 150 cc. of 90 per cent. alcohol, neutralized and mixed with 0.5 gram malachite green dissolved in 50 cc. of alcohol. With this mixture, alkalies give a purple color, which is changed to a green by acids.

Malachite green dissolves in alcohol yielding a greenish blue

[1] Read before the Washington Section of the American Chemical Society, March 14, 1901.

[2] The zinc-double-chloride of tetramethyldi-*p*-amidotriphenyl-carbinol, $(C_{23}H_{25}N_2Cl_4)_2$ +2ZnCl_2 + 2H_2O.

solution, which possesses no value as an indicator by itself, but when mixed with corallin it blends with the colors of that indicator and renders the end reaction more distinct. As only the corallin in this mixture acts as an indicator, it follows that this corallin-malachite mixture can be used in titrating only those acids and bases which give a distinct end reaction with corallin alone.

Recently I had occasion to make use of this indicator in determining the amount of alkali in a highly colored sample of beet molasses and obtained very satisfactory results. It occurred to me at once that this indicator might be used advantageously in determining the total acidity of such highly colored products as wines, vinegars and ciders, since, as is well known, the present methods are far from satisfactory in the case of red or highly colored wines. The method adopted by the Association of Official Agricultural Chemists for the determination of total acidity in wines is as follows :

" Transfer 10 cc. of the sample to a beaker, and in case of white wines add about 10 drops of a neutral litmus solution, and titrate with decinormal sodium hydroxide solution until the red color changes to violet. In case of red wines, continue adding a few drops at a time of alkali solution, until a drop of the mixture placed on delicate red litmus paper shows an alkaline reaction."

Another method in use by some chemists is to dilute 10 cc. of the wine to about 300 cc. with boiling distilled water, heat the mixture to boiling for a moment to expel carbon dioxide, add a few drops of phenolphthalein solution and titrate with decinormal sodium hydroxide solution.

Any one who has ever tried either one of the above methods with a claret or other red wine, will, I think, agree with me that the determination of the exact point of neutrality is very uncertain.

To test the corallin-malachite indicator in comparison with phenolphthalein and litmus, three samples of wine were procured : (1) a claret, as a type of red wine; (2) a Rhine wine for the white type ; and (3) a sherry for the medium color. In this experiment the following method was employed :

Transfer 10 cc. of the sample to a beaker, dilute with about 300 cc. of boiling distilled water, heat the mixture to boiling for a moment to expel all carbon dioxide, cool to about 75°, add 10 drops of the corallin-malachite solution, then add an excess of

decinormal sodium hydroxide solution, indicated by a purple color, titrate the excess of alkali with decinormal acid solution, adding the acid solution slowly until the appearance of a distinct green color. The change in color is best observed by transmitted light. A trial showed that it was easier to detect the transition from the alkali to the acid side than the reverse.

With phenolphthalein and litmus, slightly more of the indicator was used and the decinormal soda solution added slowly to the point of neutrality as near as that could be determined. The results are expressed as usual in terms of tartaric acid, 1 cc. decinormal sodium hydroxide solution = 0.0075 gram tartaric acid. The following are the results obtained :

GRAMS TARTARIC ACID IN 100 CC. OF WINE.

Wine.	Corallin Malachite.	Phenolphthalein.	Litmus.
1. Claret....................	0.840	0.995	0.890
	0.870	0.980	0.920
	0.870	0.980	....
	0.880	....	....
	0.875	....	....
Average..........	0.867	0.985	0.905
2. Rhine wine................	0.705	0.730	0.730
	0.710	0.725	0.720
	0.705	0.730	0.725
	0.695	0.735	....
	0.705	....	....
	0.705	....	....
	0.695	....	....
Average.......	0.703	0.730	0.725
3. Sherry	0.450	0.490	0.475
	0.430	0.475	0.460
	0.440	0.475	0.460
	0.445	0.475	0.460
	0.435	....	....
	0.430	....	....
Average......	0.438	0.479	0.464

The results obtained with corallin-malachite are invariably lower than those obtained with the other indicators, but this was to be expected when we consider that with the corallin-malachite the titration was made toward the acid reaction, and with the other indicators it was made toward the alkali side.

The greatest difference appears in the results on the claret or

red wine, where in case of phenolphthalein and litmus it was necessary to add a decided excess of alkali before the change of color could be detected. I am inclined, therefore, to believe that the results with corallin-malachite more nearly represent the true figure for total acidity of this sample.

To test the sensitiveness of the corallin-malachite, 5 drops of the mixture were added to 100 cc. of distilled water, when 0.1 cc. of 0.01 normal hydrochloric acid solution or 0.01 normal sodium hydroxide solution was sufficient to give a distinct acid or alkali reaction.

In the presence of other coloring-matters, slightly more of the standard solutions was required.

In consideration of the encouraging results obtained with this corallin-malachite mixture in my hands, I feel justified in recommending this indicator to the attention of chemists engaged in the analysis of wines, vinegars, ciders, and similar products.

THE ESTIMATION OF CARBONIC ACID IN WATER.

BY JOSEPH W. ELLMS AND JAY C. BENEKER.

THE estimation of carbonic acid is of considerable importance in the technical analysis of water. In the softening of water for manufacturing purposes and in the purification of public water supplies, where certain processes are employed, an accurate knowledge of the amount of this constituent is essential to a proper treatment of the water. Moreover in the sanitary analysis of sewage, of effluents from sewage purification plants, and of polluted waters generally, a determination of the amount of carbonic acid present may throw considerable light on the nature and extent of the chemical and bacterial changes which are taking place.

CONDITION IN WHICH CARBONIC ACID EXISTS IN NATURAL WATERS.

Before discussing the methods usually employed for the estimation of carbon dioxide in water, and the principles upon which these methods are based, it may be well to consider in what forms of combination carbon dioxide exists in water and to define the different terms which are used to designate them.

The carbonates which are commonly found in natural waters are those of calcium and magnesium. The normal carbonates of

these bases are, relatively speaking, but sparingly soluble in water. If, however, more than enough carbon dioxide be present to unite with the oxides of calcium and magnesium to form the compounds $CaCO_3$ and $MgCO_3$, the solubility of these salts is much increased. It is generally assumed, that when there is present one extra molecule of carbon dioxide for each molecule of calcium carbonate or of magnesium carbonate, compounds of the character of sodium bicarbonate exist, although such salts have never been isolated. These salts are presumed to have the composition represented by the formulas $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$, respectively.

The gas carbon dioxide (CO_2) is quite soluble in water and therefore may exist in natural waters in amounts greater than is required to form the bicarbonates of the alkaline earth bases which may be present. It is usually considered that carbon dioxide thus dissolved in the water exists as a true acid having the formula H_2CO_3.

From the above it is evident that there are three conditions in which carbon dioxide may be present in natural waters. If the carbon dioxide is not combined with any base, it is spoken of as "free carbonic acid;" if it is combined indirectly with the base as in the form of the bicarbonates, it is termed "half bound carbonic acid;" and if directly united to the bases as in calcium and magnesium carbonates, it is called "fixed carbonic acid." The sum of the amounts of the carbonic acid found in these three forms is usually spoken of as the "total carbonic acid." The carbonic acid that is expelled on heating aqueous solutions containing either "free" or "half-bound carbonic acid" or both is sometimes spoken of as "volatile carbonic acid."

Natural waters carry varying amounts of carbonic acid, depending on the character of the geological formations with which they have come in contact. Ground waters having probably been under greater pressure usually contain more carbonic acid than surface waters. Moreover ground waters which become exposed to the air lose the larger proportion of their free carbonic acid and may even part with some of their half-bound and fixed carbonic acid. The loss of the latter results, of course, from a precipitation of carbonates (calcium carbonate principally), as a result of the loss of some of the half-bound carbonic acid.

It was found that the ordinary distilled water of the laboratory

might contain from 6 to 10 parts per million of free carbonic acid. It was necessary to boil off 10 to 15 per cent. of the original volume of such a water in order to free it completely from the gas. A water thus freed from carbonic acid absorbs, when exposed to the air, more or less carbon dioxide depending on the amount present and on the temperature and pressure. Two samples of distilled water free from carbonic acid were exposed in beakers to the air of the laboratory in which the temperature was approximately 16° C.

	A. Free carbonic acid. Parts per million.	B. Free carbonic acid. Parts per million.
Original water.....................	0	0
After twenty-four hours...........	2.2	2.2
After forty-eight hours............	15.0	13.2
After seventy-two hours...........	0.9	0.9

The great variation in the amounts obtained was probably due to the differing quantities of carbonic acid present in the atmosphere of the laboratory on the particular day the samples were examined. On the second day a carbonic acid generator was being used in the laboratory and considerable gas was also being burned.

Waters containing large amounts of calcium bicarbonate and free carbonic acid, not only lose their free but also a portion of their half-bound carbonic acid, when exposed to the air for any length of time. The excess of calcium carbonate ($CaCO_3$) is thereby precipitated and the solution grows weaker in lime, until a state of equilibrium is reached.

The following experiments illustrate the action of a strong solution of calcium bicarbonate ($Ca(HCO_3)_2$), when exposed to the air of the laboratory.

	A. Carbonic acid in solution.			B. Carbonic acid in solution.		
	Free.	Half-bound. Parts per million.	Fixed.	Free.	Half-bound. Parts per million.	Fixed.
Original water........	52.8	109.4	109.4	52.8	109.4	109.4
After twenty-four hours	7.9	....	....	7.0	....	....
After forty-eight hours·	1.3	....	....	1.1	....	....
After seventy-two hours	0	80.7	84.5	0	80.7	84.5

Magnesium bicarbonate is much more soluble in water than calcium bicarbonate, but strong solutions show the same tendency to give up their half-bound carbonic acid as do strong solutions of calcium bicarbonate. This occurs, however, without any precipitation of magnesium carbonate ($MgCO_3$) because the latter itself is quite soluble in water.

A strong solution of magnesium bicarbonate lost all of its free and 12 per cent. of its half-bound carbonic acid in less than three days when exposed to the air of the laboratory. This solution, therefore, contained 12 per cent. of its total magnesium carbonate in the form of normal magnesium carbonate ($MgCO_3$). On the other hand the calcium bicarbonate solution, as shown above, contains only 4 per cent. of its total calcium carbonate in the form of the normal carbonate ($CaCO_3$). This illustrates the difference in degree of the affinity of solutions of these two salts for carbon dioxide.

However solutions of calcium and magnesium carbonate which contain no half-bound or free carbonic acid or only very limited amounts of the former, tend to absorb the gas from the air, and thus form the bicarbonates of these bases. Calcium carbonate solutions in time become acid (i. e., contain free carbonic acid), but the acidity is always very slight and the state of equilibrium seems to be reached when the lime is all in the form of the bicarbonate. On the contrary weak solutions of magnesium carbonate, while they absorb carbon dioxide from the air to form magnesium bicarbonate, only very slowly approach the condition where all the magnesium exists as bicarbonate; in fact the tendency seems to be for the solution to remain as a mixture of these two compounds. That these facts have a bearing on certain classes of natural waters will be shown later.

PRINCIPLES ON WHICH METHODS FOR THE ESTIMATION OF CARBONIC ACID ARE BASED WITH A DISCUSSION OF THE ERRORS AFFECTING THEIR ACCURACY.

A comparison of the three most commonly employed volumetric methods for the determination of carbonic acid in water, has been made by the writers, with the purpose of discovering, if possible, the sources of error which affected each of them, and also to learn which gave results closest to amounts actually known to be present in solution.

The oldest and best known of the three methods was suggested by Pettenkofer.[1] Trillich[2] modified this method in order to avoid certain difficulties arising in the original method, and as this modification is quite radical, the process as carried out by him

[1] *N. Rep. Pharm.*, **10**, 1.
[2] *Ztschr. angew. Chem.*, June 15, 1889, p. 337.

can be considered practically as a new method. Seyler[1] advocates what he terms the Lunge-Trillich method, which in principle differs materially from that of Pettenkofer's or Trillich's modification of Pettenkofer's method.

These three methods were those which were investigated and compared. In order to avoid confusion the three will be designated in this paper as Pettenkofer's, Trillich's, and Seyler's methods respectively.

PETTENKOFER'S AND TRILLICH'S METHODS.

The estimation of the carbonic acid in natural waters consists in determining the amount of half-bound and free carbonic acid which may be present. The estimation of the fixed carbonic acid is generally regarded as a separate determination, and is not commonly included in the statement of the results.

The principle upon which Pettenkofer based his determination depends on the action which the barium or calcium hydroxide has upon free and half-bound carbonic acid, whereby insoluble calcium and barium carbonates are formed which precipitate out of solution. Either calcium or barium hydroxide may be used, the reactions involved being of similar character.

As an excess of the precipitant is used, the portion unacted upon is determined volumetrically with a standard acid solution, and the amount of the barium or calcium hydroxide which has reacted with the free and half-bound carbonic acid can thus be determined by difference. The reaction is as follows :

$$Ca(HCO_3)_2 + CO_2 + 2BaO_2H_2 = 2BaCO_3 + CaCO_3 + 2H_2O.$$
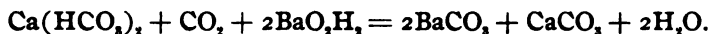
As the calcium carbonate present has been held in solution by the assistance of the half-bound molecule of carbon dioxide, it also precipitates upon the latter's removal by the barium hydroxide.

In so far as that portion of the half-bound carbonic acid, which may be present in a natural water, is combined with the magnesium carbonate to form the bicarbonate, the reaction between it and the calcium or barium hydroxide is the same as shown by the above reaction. But magnesium carbonate ($MgCO_3$) instead of precipitating out as such, reacts with the calcium or barium hydroxide and forms magnesium hydroxide, which latter, being insoluble, precipitates. The presence, therefore, of magnesium carbonate or in fact any magnesium salt causes the calcium or

[1] *Chem. News,* **70,** 104 (1894); and *Analyst,* **22,** 312 (1897).

barium hydroxide to be used up. Pettenkofer avoids the precipitation of the magnesium by the introduction of ammonium chloride, which, by forming a soluble salt of ammonium and magnesium chloride, prevents any loss of calcium or barium hydroxide. The reaction is as follows :

$$MgCO_3 + 4NH_4Cl + BaO_2H_2 =$$
$$MgCl_2(NH_4Cl)_2 + BaCO_3 + 2NH_4OH.$$
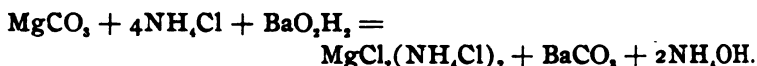
An equivalent amount of ammonium hydroxide being formed, no change in the caustic alkalinity of the sample results.

Trillich's modification of Pettenkofer's method consists in not attempting to prevent the reaction between the magnesium salts and the caustic alkali by the addition of ammonium chloride, but in allowing the precipitation to take place. From a direct gravimetric determination of the amount of the magnesium present in another portion of the sample, he is enabled to apply the proper correction to the result obtained volumetrically. Since 40 parts of magnesium oxide (MgO) would react with as much barium or calcium hydroxide as 44 parts of carbon dioxide, the correction is obtained by multiplying each part of magnesium oxide (MgO) present by 1.1 and subtracting the product from the apparent amount of carbonic acid found by the volumetric determination. Trillich's method, therefore, only differs from the original Pettenkofer method in providing another way to overcome the difficulty arising from the presence of magnesium salts.

In order to differentiate between the free, half-bound, and fixed carbonic acid, Trillich uses that portion of his solution which contains the precipitated carbonates and titrates it with hydrochloric acid and cochineal. From this he obtains the '' total carbonic acid.'' By subtracting the '' free and half-bound carbonic acid'' from this, he obtains the '' fixed carbonic acid;'' and by finding the difference between the '' free and half-bound acid'' and the '' fixed'' (equivalent to the half-bound), he estimates the ''free carbonic acid.''

It is apparent that by this means the various forms of carbonic acid may be determined in Pettenkofer's method, although the writers are not aware that originally any such differentiation was attempted.   Moreover it would seem more simple to use a method which would not involve the objectionable titration of the suspended carbonates and magnesium hydroxide. This can be done by determining the fixed carbonic acid by direct titration of a

separate sample of the water by Hehner's method, and from this all the data given can easily be deduced. In our examination of these methods we have not attempted to carry out Trillich's titration of the portion of the sample containing the precipitated carbonates.

In Pettenkofer's method and in Trillich's as well, oxalic acid is used to titrate the excess of the barium or calcium hydroxide added to the water under examination. If barium hydroxide is used Trillich recommends that to each 9 grams of the barium hydroxide, 0.5 gram of barium chloride be added in order to convert the hydroxides of sodium and potassium, which are common impurities of barium hydroxide, into chlorides. The reason for this and for the addition of barium or calcium chloride in the original Pettenkofer method, is more fully stated by Fresenius[1] as follows :

"If ...... a water contains an alkali carbonate or any other alkali salt whose acid would be precipitated by lime or baryta, a neutral solution of calcium or barium chloride must be added to decompose the same. This addition, too, prevents any inconvenience arising from the presence of free alkali in the lime or baryta water, or of magnesium carbonate in the carbonic acid water ; this inconvenience consists in the fact that oxalate of an alkali or of magnesium enters into double decomposition with calcium carbonate (which is seldom entirely absent from the fluid to be analyzed), forming calcium oxalate and carbonate of the alkali or of magnesium, which latter will of course again take up oxalic acid."

The details of the Pettenkofer process consist in taking 100 cc. of the water to be analyzed, placing it in a bottle, adding 3 cc. of barium chloride, 2 cc. of a saturated solution of ammonium chloride and 45 cc. of barium hydroxide solution. After allowing the mixture to stand about twelve hours closely stoppered, an aliquot portion of the clear supernatant liquid is pipetted off and titrated with oxalic acid. In our experiments an approximately 0.02 normal solution of sulphuric acid was used. The barium hydroxide solution was approximately 0.05 normal and the indicator employed was rosolic acid.

The Trillich method differs from the above in using 5 cc. of barium chloride in place of 3 cc., omitting the ammonium chloride and using phenolphthalein as the indicator. In titrating the

[1] " Quantitative Chemical Analysis," p. 405 (English edition, 1889).

suspended carbonates for the determination of the total carbonic acid, Trillich employs hydrochloric acid and cochineal as the indicator, as previously stated.

In carrying out these methods the following precautions have been found necessary in order to obtain uniform and consistent results.

1. The barium hydroxide solution (9 grams $BaO_2H_2.8H_2O$ and 0.5 gram $BaCl_2.2H_2O$ per liter) should be carefully filtered and kept in a bottle whose outlet to the air is provided with a U-tube containing fused calcium chloride and stick potash. A siphon tube conveniently conveys the liquid to the measuring burette. Solutions thus protected will keep for a long time without serious deterioration. A solution thus guarded from the atmospheric carbon dioxide was found at the end of fifty days to be 0.6 per cent. weaker than when first tested.

2. If oxalic acid is used, it should be frequently tested as it deteriorates rapidly. A solution containing 2.8636 grams per liter (1 cc. = 1 mg. CO_2) was found at the end of forty-five days to be 6.7 per cent. weaker and one fifty days old was 8.7 per cent. weaker.

3. Dry or well drained, ground glass-stoppered bottles with their stoppers well vaselined should be used for holding the samples. On account of the strong tendency which barium hydroxide solutions exposed to the air, show in the absorption of atmospheric carbon dioxide, the most erratic results will be obtained if the bottle stoppers are not tight-fitting.

4. Samples of water to be analyzed should properly, if at all high in free and half-bound carbonic acid, be introduced into the bottle by means of a siphon or tube, similar to the methods used in taking samples for determining dissolved oxygen.

5. After the introduction of the sample into the bottle, the other reagents should be added, the barium hydroxide solution, however, always being the last to be introduced. The barium hydroxide should be introduced by means of a long delivery tip on the burette, the lower end of which dips below the surface of the sample in the bottle. The barium hydroxide should be run in as quickly as possible and the bottle immediately stoppered and shaken.

6. The bottle should then be set aside to stand at least twelve hours and under no condition should the stopper be removed until

the clear supernatant liquid is pipetted off for immediate titration.

7. The removal of the 25 or 50 cc. of the liquid to be titrated should take place without stirring up the precipitate in the bottom of the bottle. This is extremely important and its neglect, even when only a slight amount of sediment is withdrawn, will lead to irregular and unreliable results.

8. The receptacle in which the titration takes place should be a narrow mouthed fairly long-necked flask, preferably of about 250 cc. capacity. The titration should take place immediately upon the withdrawal of the portion from the bottle and the acid should be run in quickly.

9. If the delivery of the acid can be quickly effected the larger portion should be delivered into the flask holding the barium hydroxide as soon as possible without any unnecessary shaking of the flask. The titration can then be cautiously completed. If, however, the burette delivers the acid slowly it is better to run into the empty flask the larger portion of the acid and then add the portion of the sample to be titrated. This avoids undue exposure of the caustic alkali to the air and consequently any carbonating of the barium hydroxide.

10. The standardization of the barium hydroxide solution by the acid should be carried out in a manner similar to the method employed in the titration of the sample. In standardizing the barium hydroxide solution in order to obtain its value in terms of the acid, it is necessary in the Pettenkofer method, that the titration should take place in the presence of ammonium chloride, if rosolic acid or any indicator which is at all affected by this salt, is used. Otherwise the value of the alkali in terms of the acid will be erroneous and the differences, though slight, will lead to considerable error.

In spite of the above precautions an error due to manipulation may arise on account of the extreme sensitiveness of barium hydroxide to atmospheric carbon dioxide. An average of twenty experiments made with the utmost caution, with boiled distilled water and barium hydroxide in well-ground glass-stoppered bottles, thoroughly vaselined, showed a loss of barium hydroxide equivalent to 1.5 parts per million of carbonic acid, with a range of from 1 to 3 parts per million.

Reinitzer[1] found in a solution of lime-water containing 1173.8

[1] *Ztschr. angew. Chem.*, September 15, 1894.

parts per millon of calcium oxide, carbon dioxide equivalent to
(*a*) 8.7 parts and (*b*) 9.3 parts, respectively. The results were
obtained by acidulation of the solution, expulsion of the carbon
dioxide by heating, absorption and weighing of the gas in caustic
potash. He states "we may assume the same conditions hold
good with baryta water."

The writers have found carbonic acid in calcium hydroxide solu-
tions to range from 0 to 6 or 7 parts per million, although on an
average the quantity was less than 3 parts per million. In the
case of barium hydroxide solutions we have never found over 1 part
per million of carbonic acid and the average appears to be less than
0.5 part per million. The error arising, therefore, from dissolved
carbonates in barium hydroxide solutions, in the absence of other
salts which may effect their solution, we are inclined to believe
may be usually disregarded as a source of error.

The presence of suspended carbonates in the portion of the sam-
ple being titrated, however, is a source of error which must be
carefully avoided. This arises from the direct solution of these
salts in the titrating acid ; and this is true whether oxalic acid is
used or sulphuric acid, which latter was employed by the writers.
This is shown by the following experiments.

TABLE SHOWING SOLUBILITY OF SUSPENDED CARBONATES BY
TITRATING ACID.

I. Acid Added to Alkali.

Sol. used. cc.	Containing no sus- pended carbonates. N/50 sulphuric acid. cc.	Containing suspended carbonates. N/50 sulphuric acid. cc.	Remarks.
10	3.9	5.0+	End-point indefinite with suspended car- bonates.

Sol. used. cc.	N/20 (approx.) oxalic acid. cc.	N/20 (approx.) oxalic acid. cc.	
10	2.2	2.7+	End-point indefinite with suspended car- bonates.

On another sample the following results were obtained :

I. Acid Added to Alkali.

Sol. used. cc.	Containing no sus- pended carbonates. N/50 sulphuric acid. cc.	Containing suspended carbonates. N/50 sulphuric acid. cc.	Remarks.
10	5.0	7.0+	End-point indefinite with suspended car- bonates.

II. Alkali Added to Acid.

10	5.0	7.0+	End-point indefinite with suspended car- bonates.

It will thus be seen that the presence of suspended carbonates is quite inadmissible if accurate results are to be expected.

In both Pettenkofer's and Trillich's methods, the chief disturbing element is magnesium. Its salts must either be kept in solution as in Pettenkofer's method by the use of ammonium chloride, or allowed to precipitate out and be corrected for as in Trillich's method. As the errors arising from the presence of magnesium salts are probably due to two different causes in the two methods, they will be discussed separately.

The erratic results often obtained with Pettenkofer's method are generally acknowledged. Tiemann[1] admits that duplicate results may vary from 5 to 10 parts per millon, and that the results are still more uncertain in the presence of magnesium salts. Thinking that ammonium chloride might be instrumental in holding carbonates in solution, some experiments were made to learn what effect it did have. The following experiments show the results obtained with a water which contained 59.2 parts per million of free and half-bound carbonic acid, but which contained no magnesium salts.

TABLE SHOWING EFFECT OF AMMONIUM CHLORIDE IN HOLDING CARBONATES IN SOLUTION.

No.	Sol. (approx. N/20) barium hydroxide. cc.	Saturated solution ammonium chloride. cc.	Carbonic acid (CO_2) obtained. Parts per million.
1	10	0	57.4
2	45	0	60.0
3	10	2	0.0[2]
4	20	2	0.0[3]
5	30	2	46.0
6	45	2	56.6

It will be noticed that as the concentration of the barium hydroxide solution increases, the ammonium chloride is less able to hold the carbonates in solution. Even with 45 cc. of barium hydroxide solution, the amount is still less than with the same amount of alkali where no ammonium chloride is present. It is apparent from these experiments that carbonates may be held in solution where the concentration of the barium hydroxide solution is not great enough ; and such a condition might easily arise in a water containing low amounts of magnesium but considerable

[1] " Chem. Analyses des Wassers," Tiemann.

[2] In the third experiment no loss of barium hydroxide resulted and 38.4 parts per million of fixed carbonic acid were indicated in addition.

[3] No loss of barium resulted in the fourth experiment and 1.9 parts per million of fixed carbonic acid were found in addition.

carbonic acid, which latter would use up a large proportion of the barium hydroxide added.

In order to see whether ammonium chloride was able to hold in solution all of the magnesium which might be present, the following experiments were made :

TABLE SHOWING EFFECTIVENESS OF AMMONIUM CHLORIDE IN HOLDING
MAGNESIUM SALTS IN SOLUTION.

Solution of magnesium sulphate.   Total volume of solution equal to 150 cc.

Barium hydroxide sol. (approx. N/20). cc.	Saturated solution ammonium chloride. cc.	Magnesium oxide added. Parts per million.	Magnesium oxide precipitated. Parts per million.
45	0.5	27	2.0
45	0.5	27	1.4
45	0.5	91	9.4
45	2.0	27	0
45	2.0	27	0
45	2.0	91	0

Solution of magnesium carbonate.[1]

45	2.0	15	0
45	2.0	15	0
45	2.0	15	0

It is evident that 0.5 cc. of a saturated solution of ammonium chloride is not sufficient to hold in solution all the magnesium oxide that was added. Two cc. are, however, able to hold in solution at least 90 parts per million of the oxide without any of it precipitating.

In Trillich's method the magnesium salts are allowed to precipitate as magnesium hydroxide, and are then corrected for as previously stated. It is quite evident, therefore, that unless the precipitation is complete an error is introduced into the correction. The following experiments show that this precipitation is not complete under certain conditions.

TABLE SHOWING INCOMPLETE PRECIPITATION OF MAGNESIUM HYDROXIDE BY BARIUM HYDROXIDE.

Solution of magnesium carbonate containing 15 parts per million of magnesium oxide.   Total volume of solution equal to 100 cc.

Barium hydroxide solution. cc.	Magnesium oxide precipitated. Parts per million.	Magnesium oxide not precipitated. Parts per million.
45	13.7	1.3
45	13.7	1.3
45	12.0	3.0
45	13.7	1.3
45	12.0	3.0
45	12.0	3.0
45	12.0	3.0
Average,	12.6	2.4

[1] Total volume of magnesium carbonate solution is equal to 100 cc.

From the above it will be seen that on an average 2.4 parts per million of magnesium oxide, equivalent to 2.6 parts per million of carbonic acid, were not precipitated in a solution containing 45 cc. of an approximately 0.05 normal solution of barium hydroxide in a total volume of 100 cc. From a large number of experiments made with a standard magnesium sulphate solution, it has been found that the same is true of this salt, *i. e.*, that the magnesium is but partially precipitated under certain conditions.

A large excess of barium hydroxide is necessary in order to effect practically complete precipitation, and unless this excess is maintained as the quantity of magnesium increases the quantity of magnesium which remains unacted upon will also increase.

This is well shown by the following table where constantly increasing amounts of magnesium were introduced into the solution.

TABLE SHOWING INCOMPLETE PRECIPITATION OF MAGNESIUM HYDROXIDE WITH CONTINUALLY INCREASING AMOUNTS OF MAGNESIUM SULPHATE.

Solution of magnesium sulphate. Total volume of solution equal to 100 cc.

Barium hydroxide solution. cc.	Magnesium oxide added. Parts per million.	Magnesium oxide precipitated. Parts per million.	Magnesium oxide not precipitated. Parts per million.
45	9.0	10	0
45	27.0	24	3.0
45	54.0	50	4.0
45	91.0	76	15.0

It will be noted that in the first sample, slightly more than the amount of magnesium oxide actually present appears to be precipitated. This seems to be characteristic of results obtained on samples in which the magnesium is in small amount, while the barium hydroxide is in large excess. It is due to the fact that the loss of barium hydroxide by carbonating is always greater in such cases. The error from this cause, which may be called the "error of manipulation" and the error due to non-precipitation of magnesium hydroxide, act in opposite directions, the former tending to increase the apparent precipitation and the latter to decrease it. It is probable, therefore, that the quantity of magnesium oxide not precipitated may be greater than is indicated above.

How seriously this error may affect results is shown by the following table. A standard solution was prepared and was found to contain by Trillich's method, when no magnesium salts were present, 46.2 parts per million of free and half-bound carbonic

acid. This result was the average of ten closely agreeing deter-
minations on this solution ; and the figures for the carbonic acid
found, when magnesium was present, should be compared with it.

TABLE SHOWING EFFECT OF NON-PRECIPITATION OF MAGNESIUM HYDROX-
IDE IN DETERMINATIONS OF CARBONIC ACID BY TRILLICH'S METHOD.

MgO added; equiv. to CO₂. Parts per million.	Ba₂OH₂ solu-tion. N/20(approx.). cc.	CO₂ found by titration. Uncorr. Parts per million.	Theoretical correction for MgO. Parts per million.	CO₂ cor-rected for MgO. Parts per million.	MgO equiv. to parts per million CO₂	
					Ppt'd. Parts per million.	Not ppt'd. Parts per million.
10	10	49.5	10	39.5	3.3	6.7
10	10	50.6	10	40.6	4.4	5.6
10	10	49.4	10	39.4	3.2	6.8
10	10	49.4	10	39.4	3.2	6.8
10	10	49.4	10	39.4	3.2	6.8
20	15	59.2	20	39.2	13.0	7.0
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
30	15	64.6	30	34.6	18.4	11.6
30	15	63.4	30	33.4	17.2	12.8
30	15	64.6	30	34.6	18.4	11.6
50	20	83.0	50	33.0	36.8	13.2
50	20	81.6	50	31.6	35.4	14.6
50	20	83.0	50	33.0	36.8	13.2

Note.—Amount of magnesium oxide actually present is equal
to 10/11 of amounts given as '' MgO equivalent to parts per mil-
lion of CO₂.''

The results given above of course exaggerate the error because
of the small amount of barium hydroxide and the large amounts
of magnesium. They serve to show, however, the error which
might arise from this source.

The errors affecting the accuracy of Pettenkofer's and Trillich's
methods may be briefly summed up as follows :

1. The error due to the carbonating of the barium hydroxide
as a result of manipulation. This is common to both methods
and tends to make results higher than they should be. With
careful work it can be kept very low and ought not to exceed 1
or 2 parts per million.

2. In Pettenkofer's method the solution of the carbonates by
ammonium chloride, which tends to lower the results, seems to
be the source of greatest error. The magnitude of this error ap-
pears to be governed by the concentration of the barium hydrox-
ide solution and the amount of ammonium chloride present.

3. In the Trillich method the non-precipitation of the magnesium salts, as magnesium hydroxide, tends to lower the results. The excess of barium hydroxide over and above that necessary for the reaction, appears to be fully as necessary here as in Pettenkofer's method. It is probably best to have at least an excess of from 30 to 35 cc. of 0.05 normal barium hydroxide solution for waters containing as much as 60 parts per million of magnesium oxide. The magnitude of this error may vary (even when the prescribed amount of 45 cc. of an approximately 0.05 normal barium hydroxide solution is added to each 100 cc. of water), from 2 to 5 parts per million. This amount may be exceeded with an insufficient excess of barium hydroxide.

Since the error due to unavoidable carbonating of the barium hydroxide in the course of manipulation, increases the results, and all errors arising from solubility of carbonates or non-precipitation of magnesium hydroxide lowers them, these errors tend to neutralize each other. But if the error of manipulation is kept at a minimum, the lowering of the results due to other causes, exceeds the increase, and in consequence too low results are obtained.

LUNGE-TRILLICH OR SEYLER METHOD.

This method depends on the action of phenolphthalein as an indicator in the presence of free carbonic acid and of carbonates and bicarbonates of the alkaline earth bases ; and on the assumption that in the bicarbonates of these bases there is one molecule of half-bound carbon dioxide for each molecule of fixed carbon dioxide.

Leeds[1] in this country and Trillich in Europe proposed, at about the same time, the determination of the free carbonic acid in water by titrating the sample with a solution of sodium carbonate, using phenolphthalein as the indicator. The sodium carbonate reacts with the free carbonic acid to form sodium bicarbonate. As soon as the free acid is neutralized, any further addition of sodium carbonate produces a pink color. This affords a direct means for estimating the free carbonic acid without involving the half-bound. With waters which are acid to phenolphthalein, the determination of the fixed carbonic acid by Hehner's method gives at once the half-bound carbonic acid according to

[1] This Journal, 13, 98 (1891).

the assumption stated in the preceding paragraph. With waters which are alkaline to phenolphthalein, by the determination of this "phenolphthalein alkalinity" and the "total alkalinity" obtained with lacmoid as the indicator, the amount of half-bound carbonic acid can easily be estimated. In the latter case of course free carbonic acid is absent.

Seyler, who has made a study of this method, considers it one which gives accurate results, and one which is free from many of the difficulties involved in Pettenkofer's and Trillich's methods. The chief criticism of the method seems to have been as to the correctness of the assumption for quantitative purposes, that, when a water was acid or neutral to phenolphthalein, there was present for each molecule of fixed carbonic acid, one molecule of half-bound carbonic acid ; and to the claim that when the water was alkaline to phenolphthalein, only one-half the carbonic acid in the form of the normal carbonates was determined by titrating with acid to the discharge of the color produced by this indicator.

If to 10 cc. of a cold 0.02 normal solution of sodium carbonate, phenolphthalein be added, and then a 0.02 normal solution of sulphuric acid, it will be found that only 5 cc. of the latter are required to discharge the color. The reaction is as follows :

$$2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4.$$
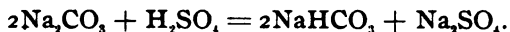
The pink color produced by the phenolphthalein in the sodium carbonate solution is destroyed when one-half the latter becomes saturated with the carbonic acid liberated by the mineral acid ; and this occurs when one-half the base has been neutralized. It is therefore evident that bicarbonates of the fixed alkalies are neutral to phenolphthalein.

The assumption that carbonates of the alkaline earth bases react in an analogous manner, is, so far as we can ascertain, correct, as the following experiments will show.

A calcium bicarbonate solution was boiled down to about one-third or one-fourth of its original volume and allowed to cool out of contact with the air. The precipitated calcium carbonate settled out, only such remaining in solution as was soluble without the presence of any free or half-bound carbonic acid. Several portions of the supernatant liquid were withdrawn and titrated with acid, using phenolphthalein as the indicator. The total alkalinity of the solution was also determined with the indicator lacmoid.

ACTION OF PHENOLPHTHALEIN AS AN INDICATOR IN A SOLUTION OF
CALCIUM CARBONATE.

No.	Calcium carbonate solution. cc.	Sulphuric acid. N/50 (approx.). A.[1] cc.	Sulphuric acid. N/50 (approx.). B.[2] cc.
1	100	1.65	3.15
2	100	1.65	3.25
3	100	1.50	3.10
Average,		1.60	3.17

A solution of magnesium carbonate acted similarly, 1.65 cc. of acid being required to discharge the pink color formed with phenolphthalein, and 3.4 cc. to obtain the end-point with lacmoid. The reaction involved in these two cases is doubtless analogous to the one which takes place in sodium carbonate solutions ; *viz.*,

$$2CaCO_3 + H_2SO_4 = Ca(HCO_3)_2 + CaSO_4.$$
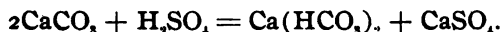
It was found that these solutions of calcium and magnesium carbonate were very sensitive to the absorption of carbon dioxide from the air, even on a very short exposure ; and also that it was extremely difficult to free them from the last traces of the half-bound carbonic acid. Only by violent and prolonged boiling and cooling out of contact with the air, could this be accomplished. A calcium carbonate solution, which after boiling was cooled in air free from carbon dioxide, required for 100 cc., 1.5 cc. of acid with phenolphthalein as the indicator, and 3.1 cc. with lacmoid. A portion of the same liquid cooled in a beaker, required 0.95 cc. of acid with phenolphthalein and 3.2 cc. with lacmoid. Magnesium carbonate solutions absorbed carbon dioxide more slowly, as has been previously pointed out.

Hot solutions of calcium carbonate and of magnesium carbonate do not react to phenolphthalein in the same manner as do these cold solutions, since in the former the bicarbonates formed by the liberation of the carbonic acid from the normal carbonates, are immediately decomposed by the heat with evolution of carbon dioxide. It is therefore possible to determine the whole of the carbonates of the alkaline earth bases even with phenolphthalein as the indicator, provided the solution is kept boiling. The same is true of the carbonates of sodium and potassium. But phenolphthalein is by no means a good indicator for this purpose and the results are much more accurately obtained with lacmoid or one of a similar character.

[1] To discharge pink color with phenolphthalein.
[2] To obtain end-point with lacmoid.

It has been considered probable that sodium carbonate in solution undergoes hydrolysis in the following manner.

$$Na_2CO_3 + H_2O = NaHCO_3 + NaOH.$$
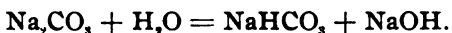
As the sodium bicarbonate thus formed supplies no hydrogen ions, and the sodium hydroxide is dissociated producing a large number of hydroxyl ions, the solution is therefore quite strongly alkaline. To phenolphthalein it exhibits the alkalinity characteristic of caustic alkaline solutions. It may be that a similar hydrolysis takes place in the case of calcium carbonate and magnesium carbonate solutions.

$$2CaCO_3 + 2H_2O = Ca(HCO_3)_2 + Ca(OH)_2.$$
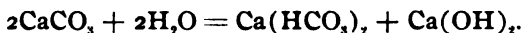
If this does occur it readily explains why calcium and magnesium carbonate solutions are alkaline to phenolphthalein and why they show the same evidence of the presence of hydroxyl ions as in the case of sodium carbonate solutions.

The essential details of the Seyler process are as follows:

The free carbonic acid is determined by placing 100 cc. of the sample in a glass cylinder with 25 to 30 drops of a neutral solution of phenolphthalein. To the sample is then added a solution of sodium carbonate (0.05 or 0.02 normal solution may be used), stirring carefully and thoroughly until a faint permanent pink color is obtained.

The following precautions have been found desirable if accurate results are to be expected.

1. The titration can conveniently take place in a short Nessler cylinder. The writers used a tube approximately 18 cm. long by 3 cm. in diameter, graduated for 50 and 100 cc. The stirring rod used was bent at its lower end into the form of a circle and then turned so as to stand at right angles to the rod. A comparison cylinder containing the same amount of water as there was in the titrating cylinder, was found to aid in the determination of the end-point.

2. The larger part of the sodium carbonate solution should be added quickly and the strong pink color formed should be discharged by stirring and mixing with the rod. The titration can then be cautiously completed. When the color remains permanent the titration is complete. The sodium carbonate solution should be prepared with freshly ignited sodium carbonate and with water which has been thoroughly boiled and cooled out of

contact with the air. The exposure of this solution to the air should be avoided as much as possible as sodium bicarbonate is readily formed, which renders it useless for this titration where accurate results are desired.

3. With waters that are high in free and half-bound carbonic acid it is better to use less than 100 cc. for the titration, especially if 0.02 normal sodium carbonate solutions are used. With such a water, care is necessary in transferring the sample to the cylinder in order to avoid loss of carbonic acid. Too vigorous stirring of the water is also to be avoided for the same reason.

The fixed carbonic acid, from which the half-bound acid is estimated, is determined according to the method of Hehner. Seyler uses methyl orange as the indicator for this titration, but the writers employed lacmoid. The accuracy of this process[1] is well-known and need not be here discussed.

In the absence of free carbonic acid in a water, the half-bound may equal the fixed, in which case it would be neutral to phenolphthalein. If, however, the water is alkaline to phenolphthalein, the half-bound carbonic acid does not equal the fixed ; or in other words a portion of the carbonates of the bases exist in solution without the assistance of any half-bound carbonic acid. In such a case the half-bound acid is obtained by first determining the fixed carbonic acid by means of lacmoid. From this is deducted an amount of carbonic acid equal to twice the quantity indicated by the acid required to discharge the pink color produced by phenolphthalein. The difference is the amount of half-bound carbonic acid which is present. These titrations may be made on the same sample, in which case the " phenolphthalein alkalinity" is first determined and then followed by the titration with lacmoid ; or they may be made on separate samples.

The principles on which the above procedure is based have been pointed out above.

These titrations involve no especial difficulties and can be easily and quickly carried out. Approximately 0.02 normal solutions of sulphuric acid were used by the writers and the same strength of sodium carbonate solution. Seyler has prepared a series of formulas for calculating the results, which simplifies the work somewhat. If results are obtained with 100 cc. of the sample

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[1] J. W. Ellms : This Journal, 21, 359.

and the reagents employed are 0.02 normal the following formulas express the results in parts per million.

I. For waters acid or neutral to phenolphthalein :

Free carbonic acid $= 4.4p$
Fixed or half-bound carbonic acid $= 4.4m$
Volatile carbonic acid $= 4.4\,(m + p)$
Total   "   " $= 4.4\,(2m + p)$

$p =$ cc. 0.02 normal sodium carbonate solution required to produce a pink color with phenolphthalein in 100 cc. of the water ; and

$m =$ cc. 0.02 normal sulphuric acid solution required to obtain the end-point with methyl orange or lacmoid in the same volume of water.

II. For waters alkaline to phenolphthalein :

Fixed carbonic acid $= 4.4\,m$
Half-bound or volatile carbonic acid $= 4.4\,(m - 2p')$
Total carbonic acid $= 4.4\,(2m - 2p')$

$m =$ cc. 0.02 normal sulphuric acid solution required to obtain end-point with methyl orange or lacmoid in 100 cc. of the sample.

$p' =$ cc. 0.02 normal sulphuric acid required to discharge the pink color produced by phenolphthalein in 100 cc. of the sample.

There is a third case in which free carbonic acid might exist in a solution containing free mineral acid and for which Seyler has given a method with its corresponding formulas for calculating the results. But such a condition would seldom be found in natural waters and need not here be described.

The errors affecting the accuracy of Seyler's method are those which arise in part from the determination of the free carbonic acid. The end-point in the titration of the sample with sodium carbonate and phenolphthalein is not entirely satisfactory. The results obtained are usually low, but with care and practice the error from this source should be less than 2 to 3 parts per million, even with considerable amounts of carbonic acid, and on small amounts it is less still.

The error due to the determination of the fixed carbonic acid, from which the half-bound is derived, arises from those errors involved in the carrying out of Hehner's method and which in good work ought not to exceed 1 to 2 parts per million.

COMPARISON OF THE THREE METHODS ON WATERS CONTAINING KNOWN AND UNKNOWN AMOUNTS OF CARBONIC ACID.

The comparison of the results obtained with known solutions of carbonic acid indicate the relative and actual accuracy of these three methods. Solutions containing known amounts of free and half-bound carbonic acid were prepared by neutralizing partially or wholly measured quantities of a 0.02 normal solution of sodium carbonate with a 0.02 normal solution of sulphuric acid. Solutions of calcium and magnesium salts were introduced in order that these bases might be present and thus produce an artificial water having approximately the same composition as natural waters.

The first table shows the amount of free carbonic acid obtained in a solution known to contain 44 parts per million. This solution contained no calcium or magnesium salts. The term "Trillich method" has been used in the column headings of the following tables in the sense in which it was defined in the first portion of this paper. Strictly speaking, in the absence of magnesium salts where the use of ammonium chloride is unnecessary, the columns could have been headed "Pettenkofer method;" but to avoid confusion the definitions first given have been adhered to.

TABLE SHOWING FREE CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 44 PARTS PER MILLION.

No.	Trillich method. Parts per million.	Seyler method. Parts per million.
1	41.7	44.2
2	43.7	44.7
3	42.2	44.2
4	40.8	43.8
5	42.7	44.0
6	41.7	43.6
7	40.8	44.4
Average,	42.0	44.0

When free and half-bound carbonic acid were present together in known amounts the following results were obtained :

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN A SO-
LUTION KNOWN TO CONTAIN 8 PARTS FREE AND 40 PARTS HALF-
BOUND CARBONIC ACID. (FREE AND HALF-BOUND
ACID EQUALS 48 PARTS PER MILLION.)

| No. | Trillich method. Free and half-bound acid. Parts per million. | Seyler method. | | |
		Free acid. Parts per million.	Half-bound acid. Parts per million.	Free and half-bound acid. Parts per million.
1	47.0	7.0	40.8	47.8
2	46.1	6.2	41.3	47.5
3	46.1	6.6	41.3	47.9
4	47.0	7.0	41.3	48.3
5	47.0	7.9	41.3	49.2
6	45.0	7.9	41.3	49.2
7	45.4	7.5	41.3	48.8
8	46.1	7.9	40.8	48.7
9	46.1	7.0	41.3	48.3
10	46.1	7.9	41.3	49.2
Average,	46.2	7.3	41.2	48.5

The following table shows the results obtained with these
methods, when the solution contained double the amount of free
and half-bound carbonic acid as was present in the solution from
which the figures in the preceding table were obtained.

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN A SO-
LUTION KNOWN TO CONTAIN 16 PARTS FREE AND 80 PARTS HALF-
BOUND CARBONIC ACID. (FREE AND HALF-BOUND
ACID EQUALS 96 PARTS PER MILLION.)

| No. | Trillich method. Free and half-bound acid. Parts per million. | Seyler method. | | |
		Free acid. Parts per million.	Half-bound acid. Parts per million.	Free and half-bound acid. Parts per million.
1	92.2	15.8	78.2	94.0
2	91.0	14.5	81.1	95.6
3	91.0	14.1	81.1	95.2
4	90.5	14.5	80.2	95.2
5	90.5	15.0	80.2	94.7
Average,	91.0	14.8	80.1	94.9

No attempt has been made in our work with Pettenkofer's and
Trillich's methods to differentiate by titration (according to
Trillich's method), the free carbonic acid from the half-bound.
Assuming, however, that the half-bound acid in the above solu-
tion is, as shown by the average, 80.1 parts per million, then the
free carbonic acid by Pettenkofer's or Trillich's method would be
91 parts minus 80.1 parts or 10.9 parts per million.

In the following table are shown comparisons made with solutions containing known amounts of free and half-bound carbonic acid, and which also contained varying but known amounts of magnesium salts.

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN SOLUTIONS KNOWN TO CONTAIN 4.9 PARTS FREE AND 41.6 PARTS PER MILLION OF HALF-BOUND CARBONIC ACID, AND WITH VARYING AMOUNTS OF MAGNESIUM SULPHATE. (FREE AND HALF-BOUND ACID EQUALS 46.5 PARTS PER MILLION.)

No.	Magnesium sulphate present equivalent to carbonic acid. Parts per million.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method. Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
1	10	44.6	43.9	4.6	48.2	45.8
2	10	43.1	43.9	...	....	....
3	10	43.1	44.4	...	....	....
4	20	41.5	45.6	4.3	41.2	45.5
5	20	44.6	44.2	4.0	41.9	45.9
6	40	44.6	43.3	4.0	42.6	46.6
7	40	43.1	40.4	4.6	41.2	45.8
8	40	46.0	40.4	...	....	....
Average,		43.8	43.2	4.3	41.6	45.9

Assuming as in the preceding tables that the half-bound carbonic acid is on an average 41.6 parts per million in the above solution, then the Pettenkofer results indicate 2.2 parts per million of free carbonic acid and the Trillich results 1.6 parts per million.

Comparisons were also made on natural waters containing unknown amounts of free and half-bound carbonic acid. The first table given below shows the results obtained on a sample of Ohio river water by the three different methods. This sample of water contained by a gravimetric determination 10 parts per million of magnesium oxide equivalent to a correction to be applied to the Trillich figures of 11 parts per million.

TABLE SHOWING AMOUNT OF CARBONIC ACID FOUND IN OHIO RIVER WATER BY THE THREE METHODS.

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method. Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
1	14.9	15.4	0.6	16.2	16.8
2	14.9	16.8	0.4	16.4	16.8

No	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method.		
			Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
3	13.4	16.1	0.4	16.2	16.6
4	14.4	16.8	0.4	16.6	17.0
5	14.4	16.8	0.6	16.6	17.2
6	14.4	16.1	0.6	16.2	16.8
7	13.4	16.8	0.4	16.4	16.8
8	14.9	15.4	0.4	16.6	17.0
9	13.2	16.8	0.4	16.6	17.0
Average,	14.2	16.3	0.4	16.4	16.8

The following well water was also examined and is given as an illustration of a water highly charged with carbonic acid and containing a large quantity of mineral salts, especially those of magnesium. A gravimetric determination of the calcium and magnesium, and also of the sulphuric acid, gave the following results.

<div align="center">WELL WATER.</div>

Parts per million.

Lime (CaO) 378
Magnesia (MgO) 128
Sulphuric acid (SO_3) 351

The free and half-bound carbonic acid were determined by the three volumetric methods and the results obtained are shown in the following table:

TABLE SHOWING AMOUNT OF CARBONIC ACID FOUND IN A WELL WATER BY THE THREE METHODS.

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method.		
			Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
1	241	242.4	63.4	176.4	239.8
2	241	236.5	66.9	176.4	243.3
3	241	236.5	68.6	176.4	245.0
4	241	246.3	65.1	177.4	242.5
5	238	242.4	68.6	176.4	245.0
Average,	240.4	240.8	66.5	176.6	243.1

As would be expected the variation in the above results is in some cases considerable, but the greatest difference is less than 10 parts per million and the greatest variation from the mean of all the results is less than 5 parts per million.

The results of the above analysis were all obtained on waters which when cold reacted neutral or acid to phenolphthalein. There is one other class of waters, which when cold react alkaline to phenolphthalein, and which in consequence require a modification of Seyler's method as previously described. The number of waters belonging to this class does not seem to be at all large, and the writers have never examined but one water which showed this feature. Seyler states that pure sea water is alkaline to phenolphthalein. He gives the following analysis:

Parts per million.

Free carbonic acid	0
Half-bound carbonic acid	44.0
Fixed carbonic acid	51.7
Total carbonic acid	95.7

He also states that he has found well waters which upon standing exposed to the air for some time, reacted alkaline to phenolphthalein, and that such waters contained considerable magnesium carbonate.

The writers have found that at certain times the Mississippi river water is alkaline to phenolphthalein. How long such periods last or at what seasons of the year they occur, we have not had the opportunity to determine. It is quite probable that the so-called "alkali waters" of the Western plains would react alkaline to phenolphthalein as they contain carbonates of sodium. It has been noted that water which has stood in the iron pipes of the laboratory for some time, will, when first drawn, react alkaline to phenolphthalein. This is due probably to the free carbonic acid and bicarbonates in the water reacting with the iron of the pipe to form carbonate of iron, and thus leaving in solution small amounts of normal calcium and magnesium carbonates.

The water examined by us, which reacted alkaline to phenolphthalein, was a mixed sample of Mississippi river water. The samples were taken during the month of September, 1900, opposite Quincy, Illinois. When examined it was found to give a strong pink color with phenolphthalein. Its average approximate composition was as follows:

Parts per million.

Lime (CaO)	35.6	equivalent to 63.5 parts $CaCO_3$.	
Magnesia (MgO)	16.0	" " 33.6 " $MgCO_3$.	
Sulphuric acid (SO_3)	7.2		
Chlorine (Cl)	6.3		
Fixed carbonic acid (CO_2)	39.8	" " 90.4 " when expressed in the form of calcium carbonate.	

From a consideration of these results it is more than probable that the magnesium was present partly as normal magnesium carbonate ($MgCO_3$), and the calcium as calcium bicarbonate. Only a limited quantity of the sample was available for experimental purposes. The following table shows the average of the results obtained in determining the carbonic acid by the three volumetric methods.

CARBONIC ACID OBTAINED IN A SAMPLE OF MISSISSIPPI RIVER WATER.

Pettenkofer method.		Trillich method.		Seyler method.	
Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.
0	0	0	34.6	0	35.4

Seven different portions of this water treated according to Pettenkofer's method showed that in no instance was any barium hydroxide used up, and that on an average only 60 parts per million (expressed in terms of $CaCO_3$) of carbonates were precipitated out, which still left in solution about 30 parts per million. The reason for this is not clear, but it is probable that the ammonium chloride used was one factor which was instrumental in holding a portion of the carbonates in solution. Whether the dissolved organic matter, which was in considerable amount, was another cause of such unusual results, we are unable to state.

An artificial water prepared so as to contain approximately the same amounts of calcium and magnesium carbonates as were present in the Mississippi river sample, gave the following results:

	Pettenkofer method.		Trillich method.		Seyler method.	
No.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.
1	0	27.9	0	31.6	0	31.7
2	0	29.4	0	31.6	0	32.2
Average,	0	28.6	0	31.6	0	31.9

This water contained 11 parts per million of magnesium oxide, equivalent to a correction in the Trillich method of 12 parts per million.

The tendency here is for Pettenkofer's method to give low results, but the carbonates are not affected to the extent that they were in the river water.

CONCLUSIONS.

From a consideration of the data obtained in this investigation, it appears that the Lunge-Trillich or Seyler method is the most accurate of the three volumetric methods. The "free and half-bound carbonic acid" as determined on known amounts by this method is on an average less than 1 per cent. too low and shows a possible range of less than ± 3 per cent. The accuracy of the determination of the "free carbonic acid" is somewhat less, and although the percentage error for low amounts is rather high, the variation from the actual amount is not more than 2 to 3 parts per million. These results are always too low and introduce into the determination of the "volatile carbonic acid" the larger proportion of the error.

Trillich's modification of Pettenkofer's method is less accurate than the Seyler method but more accurate than the Pettenkofer. Results obtained with either Pettenkofer's or Trillich's method are almost always too low. They probably give figures which are on an average between 5 and 10 per cent. too low. While Trillich's method gives more uniform results than Pettenkofer's the figures appear to be about 5 per cent. too low, and they may be as much as 10 or 12 per cent. too low.

Pettenkofer's method is inclined to give still lower results and although those obtained seemed to be only from 1 to 2 per cent. lower than those obtained with Trillich's method, yet it appears somewhat unreliable and one in which under some conditions extremely erratic results are likely to occur. With very low amounts of carbonic acid the percentage error in both Pettenkofer's and Trillich's methods are much greater than those stated above, although it may only represent an actual difference of from 3 to 4 parts per million.

For ease and rapidity of manipulation, for avoidance of difficulties arising from the presence of magnesium salts, and for its greater accuracy, the Lunge-Trillich or Seyler method is, in the opinion of the writers, to be preferred to either of the other two volumetric methods.

LABORATORY "COMMISSIONERS OF WATER WORKS,"
CINCINNATI, OHIO.

NOTES.

Notes on the Paper by Hiltner and Thatcher.[1]—The method proposed in the paper is a modification of the Sachs-Le Docte modification of Pellet's " instantaneous aqueous diffusion method."[2] The device of weighing any convenient quantity of pulp and adding thereto the proper proportionate quantity of a mixture of water and lead acetate solution, first suggested by Walawski in 1894, has been practiced in this laboratory for the two seasons past. In 1899, or earlier, a special burette was obtained, the same being made to order for the purpose, after a drawing and description devised and wrought by Dr. G. L. Spencer.

The ideas contained in the paper that are new, other than those mentioned above, seem to be principally in regard to the allowance to be made for the liquid matter in the beet pulp, and the means of determining the amount of allowance to be made. It seems that the authors of the paper are in error :

First, because they base their corrections on the percentage of water in the beet, instead of on the percentage of liquid (juice) in the beet. The substances (sugar, etc.) dissolved in the water contained in the beet must necessarily increase the volume of that water as calculated from its weight at a given temperature. (See p. 309).

Second, because their determinations of water contained in beets, as reported on pages 308 and 309 are higher than is indicated by previous results of determinations of the amount of fiber contained in beets. For example, if in Table I we make the following additions, we obtain totals that are too high.

	Per cent.	Per cent.	Per cent.	Per cent.
Average water	84.64	83.05	82.10	81.25
Average sugar	9.00	11.00	13.00	14.00
Average non-sugar (calculated)	2.25	1.94	2.29	2.47
Total.....	95.89	95.99	97.39	97.72
Difference (marc).....	4.11	4.01	2.61	2.28

The non-sugar is here obtained by calculation from the percentage of sugar, assuming a purity coefficient of 80 in the first

[1] See this Journal, **23**, 299.
[2] See Spencer's " Handbook for Beet-Sugar Chemists," p. 181.

case and 85 in the other three cases. As little as 4 per cent. of marc is possible, but 2.61 per cent. is doubtful, and 2.28 per cent. still more so. Making the same calculations from data given in Table II, we obtain:

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Average water........	81.74	82.00	84.51	83.27	81.89	81.21
Average sugar........	12.70	11.90	8.60	11.80	12.30	13.60
Average non-sugar...	3.18	2.98	2.15	2.95	3.08	3.40
Total....	97.62	96.88	95.26	98.02	97.27	98.21
Difference (marc)....	2.38	3.12	4.74	1.98	2.73	1.79

The percentages of non-sugar given in this table are calculated, assuming a purity of 80 for the juices of the beets.

From the data obtained in these two tables, the authors conclude: "All of these figures indicate that for beets, most of which contain between 8 per cent. and 14 per cent. of sugar, 83 per cent. might be assumed as an average water factor without there being a variation in any individual case of more than 3 per cent."

In the case of pulp having 83 per cent. of water, 26.048 grams of it contain 21.62 grams of water measuring 21.62 Mohr's cc. at 17.5° C. Assuming a purity coefficient of 80, a beet containing 8 per cent. of sugar would contain 10 per cent. of soluble solids, while one containing 14 per cent. of sugar would contain 17.5 per cent. of soluble solids. If a solution be prepared for analysis by mixing 26.048 grams of pulp with 78.38 Mohr's cc. of water measured at 17.5° C., we would have in the two cases :

	Beets containing 8 per cent. sugar. Grams.	Beets containing 14 per cent. sugar. Grams.
Water in pulp....................	21.62	21.62
Soluble solids in pulp............	2.6048	4.5584
Water added....................	78.38	78.38
Total....	102.6048	104.5584
Percentage of soluble solids in the mixture.......................	2.54	4.36
Specific gravity of the liquid in the mixture....................	1.00992	1.01714
Volume of the liquid in the mixture, Mohr's cc. at 17.5° C	101.60	102.80

Working by this method, therefore, the volume of the solution would be 1.6 to 2.8 per cent. too great under the conditions of these two examples. The soluble solids materially increase the volume of the solution.

The ordinary manner of arriving at the allowance to be made in analyses by this method is to assume an average juice content

for the beets, and allow for the volume of the assumed quantity of juice of average density.

In the case of beets containing 95 per cent. of juice, 26.048 grams of pulp contain 24.7456 grams of juice, or 23.60 cc. when the juice is 12° Brix, and 22.84 cc. when the juice is 20° Brix.

In case of 90 per cent. juice, 26.048 grams of pulp contain 23.4432 grams of juice ; or 22.36 cc. and 21.64 cc. of liquid in the cases of 12° Brix and 20° Brix juice respectively. Assembling these data in the form of a table we have :

VOLUME OF JUICE CONTAINED IN 26.048 GRAMS OF PULP.

	12° Brix. cc.	20° Brix. cc.	Means. cc.
95 per cent. juice	23.60	22.84	23.22
90 per cent. juice	22.36	21.64	22.00
Means	22.98	22.24	22.61

A quantity of liquid of 16° Brix that measures 22.61 cc. at 17.5° C. weighs 24.0944 grams and contains 3.8550 grams of solids. 23.6 cc. of liquid, 12° Brix, weigh 24.7456 grams and contain 2.9694 grams of solids. 21.64 cc. of liquid, 20° Brix, weigh 23.4432 grams and contain 4.6886 grams of solids.

If 26.048 grams of beet pulp of the qualities just described be mixed at 17.5° C. with water equivalent to 100 cc., less the volume of liquid contained in the pulp, mixtures of the following compositions and properties will be obtained :

	Beets containing 95 per cent. of juice of 12° Brix.	Beets containing 90 per cent. of juice of 20° Brix.	Beets containing 92.5 per cent. of juice of 16° Brix.
	Grams.	Grams.	Grams.
Water contained in pulp	21.7762	18.7546	20.2394
Added water	76.40	78.36	77.39
Soluble solids in pulp	2.9694	4.6886	3.8550
Total	101.1456	101.8032	101.4844
Percentage of soluble solids in the mixture	2.94	4.61	3.80
Specific gravity of the liquid in the mixture	1.0115	1.01814	1.01491
Volume of the liquid in the mixture, Mohr's cc. at 17.5° C	99.996	99.989	99.993

The quantities of water added in the first two cases, vary

approximately 1 cc. from the last mean case. If we use 77 cc. in each case as directed by the Sachs-Le Docte method, irrespective of the quality of the beets, we have errors as follows in two extreme cases :

	Beets containing 95 per cent. of juice of 20° Brix. Grams.	Beets containing 90 per cent. of juice of 12° Brix. Grams.
Water contained in pulp ············	19.7965	20.6300
Water added (Sachs-Le Docte)······	77.0000	77.0000
Soluble solids in pulp·············	4.9491	2.8132
Total····	101.7456	100.4432
Percentage of soluble solids in the mixture···························	4.86	2.80
Specific gravity of the liquid in the mixture···························	1.01914	1.01094
Volume of liquid in the mixture in Mohr's cc. at 17.5° C ·············	99.83	99.35

If we take the other two extremes, we have for

	Beets containing 95 per cent of juice of 12° Brix. Grams.	Beets containing 90 per cent. of juice of 20° Brix. Grams.
Water contained in pulp············	21.7762	18.7546
Water added (Sachs-Le-Docte)······	77.0000	77.0000
Soluble solids in pulp··············	2.9694	4.6886
Total····	101.7456	100.4432
Percentage of soluble solids in the mixture ···························	2.92	4.67
Specific gravity of the liquid in the mixture ···························	1.01142	1.01838
Volume of the liquid in the mixture in Mohr's cc. at 17.5° C··········	100.60	98.63

In these extreme cases the error varies from 0.17 cc. to 1.37 cc. ; or rather, from 0.6 cc., too great a volume, to 1.37 cc., too small a volume. The increase of the volume of the water contained in the pulp, due to matter dissolved in it, is not appreciably lessened when the liquid is diluted to 100 cc. It therefore seems that the error attending the use of the Sachs-Le Docte allowance of 23 cc. for the liquid contained in the pulp will not be greater than that attending the method of Hiltner and Thatcher. This is especially true when 26.048 grams of pulp are mixed with 177 cc. of water instead of 77 cc.

In the case of beets that are both very rich and very dry because of their conditions of growth or storage, the proportion of water to be added to a given weight of pulp should undoubtedly be increased.

The balance mentioned on page 314 I believe to be the "Steinke Matador, Pracisionswaage ohne Benutzung von Gewichten." We have tried this balance in this laboratory for the purpose mentioned and have found it to be wholly inaccurate and useless for this purpose.

On page 309, the authors of the paper are led to make an unjust criticism of the method proposed by Walawski, because of a typographical error made by us in the translation of Sachs' paper. Walawski recommended the addition of a weight of water equal to 3 times the weight of the pulp and not 3.6 times the weight of the pulp as stated.

In the closing paragraphs of their paper, the authors describe an application of their method to the analysis of beet juices, which needs a word of comment.

They state that "A water factor of 85 per cent. was adopted." This implies that the beet juices were assumed to contain 15 per cent. of total solids, which corresponds to a specific gravity of 1.06133. 26.048 grams of juice of this density measure 24.54 Mohr's cc. at 17.5° C. At 30° C. the specific gravity would be somewhat less; the volume would be approximately 24.63 Mohr's cc. It is difficult to understand how the excellent comparative results would have been obtained by the authors of this paper by allowing only 22.14 cc. for the increase in the volume of the mixture due to the beet juice.   E. E. EWELL.

DIVISION OF CHEMISTRY, U. S. DEPARTMENT
OF AGRICULTURE, WASHINGTON, D. C.,
March 20, 1901.

NEW BOOKS.

THE TESTING AND VALUATION OF RAW MATERIALS USED IN PAINT AND COLOUR MANUFACTURE. BY M. W. JONES, F.C.S. A book for the laboratories of colour works. 88 pages. Price, $2.00.

Excepting a chapter on oils, this book is devoted to a general survey of the most important inorganic raw materials used by the trade. The subjects treated under separate headings are: China clay, ammonium hydrate, acids, ultramarine, oils, and the compounds of aluminium, iron, potassium, sodium, chromium, tin, copper, lead, zinc, manganese, arsenic, antimony, calcium, barium, cadmium, mercury, cobalt, and carbon.

Suitable tests are given for the detection of impurities and adulterants; and the schemes of analysis are familiar ones, simple,

accurate, and precisely described. Gravimetric methods are given in nearly every case supplemented in many instances by volumetric. The chapter on oils is confined to the estimation of fatty acids in Turkey-red oil, and to the detection in linseed oil of mineral, resin, raw or boiled oils.

The book is an excellent compilation which will undoubtedly find favor in the laboratory. It has an index.

C. W. PARMELEE.

CHRISTIAN FRIEDRICH SCHÖNBEIN, 1799–1868. Ein Blatt zur Geschichte des 19. Jahrhunderts, von GEORG W. A. KAHLBAUM und ED. SCHAER. 2 vols., Leipzig, 1899–1901. Vol. I, 230 pp. Portrait; Vol. II, 326 pp. (Viertes und sechtes Hefte Monographien aus der Geschichte der Chemie, herausgegeben von Georg W. A. Kahlbaum.)

These two volumes contain the life history of that remarkable man who will always be remembered as the discoverer of four notable things of diverse nature in their physical and chemical aspects, the Passivity of Iron, Ozone, Guncotton and Collodion.

The author, who occupies the chair of chemistry in the University of Basle, has enjoyed the best opportunities for gathering the data needed for his work; from the three living daughters of Schönbein, from his friends both in Germany and in England, he has had for study not less than 1600 letters, and through libraries and personal friends he has consulted 350 of Schönbein's printed papers. And with these aids he has portrayed the man in his scientific pursuits and social life.

Schönbein, who was born 18th October, 1799, in what is now known as the kingdom of Würtemberg, inherited a love for chemistry from his father, who was a dyer and as such occupied with problems requiring chemical knowledge. At the age of twenty-one he entered the manufactory of chemicals of Dr. J. G. Dingler, in Augsburg, where his daily labor extended from 6 A.M. to 7 P.M., leaving him only from 4 to 6 A.M. and from 7 to 10 P.M. for private study and recreation. For this he received board and lodging and 200 to 300 florins a year. Dingler had just begun to publish his *Polytechnisches Journal.* (1820–1901).

After studying some semesters at the Universities of Tübingen and Erlangen, he secured a position as teacher of physics, chemistry, and mineralogy in the educational institution founded a few years before by Friedrich Fröbel, of kindergarten fame. In 1826 we find him a teacher in London, and in 1828 again on the con-

tinent, teaching experimental chemistry at the University of Basle, where he was made professor of chemistry and physics in 1835.

We cannot in a book-review further follow his fortunes in such detail; suffice it to say that he made all his notable discoveries after he had reached the age of 36, and while holding the chair just named; he read his paper on the passivity of iron before the Natural History Society of Basle in 1835; he discovered ozone in 1839 and worked at it until 1860; and his discoveries of guncotton and of collodion were made between 1846 and 1853.

The long studied and puzzling problems connected with ozone and "antozone," that occupied so much of his life are here set forth with a minuteness not elsewhere found; the claims of others to the discovery of guncotton are dwelt upon fully, and it is significant to read that Schönbein reaped about $20,000 from his discovery, while Alfred Nobel gained no less than $10,000,000.

Schönbein enjoyed the friendship of nearly all his contemporaries in the physical sciences; his correspondence with Faraday forms a volume edited by Kahlbaum and Darbishire and published at London in 1899.

The volumes under review form so important a contribution to the history of chemistry that no library can well afford to be without them. H. CARRINGTON BOLTON.

THE ELEMENTARY PRINCIPLES OF CHEMISTRY. By A. V. E. YOUNG. 12mo. xiv + 252 pp. New York: D. Appleton & Co. 1901. Price, $1.20.

The author of this book desires "that the first notion of a topic should come to the student through his own observation" and provides, with this end in view, a relatively large amount of laboratory work, more of which is quantitative in character than is usual in elementary courses.

In a pamphlet entitled "Suggestions to Teachers," which accompanys the book, Professor Young points out the advantages of the plan which, he advocates, indicates the amount of time required—eight hours per week for thirty-five weeks,—and gives helpful advice to teachers. The greater part of the time is, evidently, to be devoted to the laboratory work.

The introductory chapters discuss matter, energy, chemical and physical properties, the fundamental laws of chemical action, equivalent and combining weights and methods for obtaining

them, equations, the relation between the volume, pressure, and temperature of gases, etc. Then follows a chapter on the atomic and other theories, the distinction between the theories and the facts, which they are intended to explain being clearly shown. The author has been very successful in presenting, with a limited use of theoretical considerations, the prevailing views of chemists.

The remaining two-thirds of the book give a clear, and sufficiently full description of twenty-five elements, and some of their compounds, the order of treatment being that of their increasing combining weights. The writer believes that this part of the subject would have been of more value, if enough elements had been described to show more clearly the relation of elements belonging to the same groups.

Part second, which may also be obtained separately, contains directions for work in the laboratory. Illustrations of twelve distinguished chemists and physicists are an attractive feature of the book.   L. B. HALL.

BOOKS RECEIVED.

The Elementary Principles of Chemistry. By A. V. E. Young. New York : D. Appleton & Co. 1901. xiv + 106 pp. Price, $1.20.

Suggestions to Teachers ; designed to accompany "The Elementary Principles of Chemistry." By A. V. E. Young. New York : D. Appleton & Co. 1901. 48 pp.

Pure Air, Ozone and Water. A practical treatise of their utilization and value in oil, grease, soap, paint, glue, and other industries. By W. B. Cowell. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. 85 pp. Price, $2.00.

The Testing and Valuation of Raw Materials used in Paint and Colour Manufacture. By M. W. Jones, F.C.S. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. 88 pp. Price, $2.00.

The Manufacture of Lake Pigments from Artificial Colours. By Francis H. Jennison. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. 136 pp. Price, $3.00.

Iron Corrosion. Anti-fouling and Anti-corrosive Paints. By Louis Edgar Andés. Translated from the German by Charles Salter. London : Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1900. viii + 275 pp. Price, $4.00.

Glue and Glue Testing. By Samuel Rideal. D.Sc.Lond. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. viii + 144 pp. Price, $4.00.

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PROCEEDINGS.

CONTENTS.

The Chemistry of Materials Used in Perfumery and Kindred Arts, by T. C. Stearns. Decomposition of the Chlorides of the Alkali Metals, with Exhibition of Crystals, by C. W. Volney. Metallic Soaps from Linseed Oil : an Investigation of Their Solubilities in Certain of the Hydrocarbons, by H. T. Vulté and Harriet W. Gibson. *a.* On the Heat of Combustion as a Factor in the Analytical Examination of Oils; *b.* The Heats of Combustion of Some Commercial Oils, by H. C. Sherman and J. F. Snell. By-Laws for Governing the New York Section of the American Chemical Society.

Physics and Faith, by H. Carrington Bolton. The Solubility of Gypsum in Aqueous Solution of Sodium Chloride, by F. K. Cameron. Equilibrium between Carbonates and Bicarbonates in Aqueous Solution, by F. K. Cameron and J. L. Briggs.

Physical Reactions and the Mass Law, by A. T. Lincoln. The Manufacture of Carborundum at Niagara Falls, by O. W. Martin. The Nature of the Enzymes, by J. H. Kastle. The Alkalimetric Factors of Some Alkaloids, by H. M. Gordin. Atomic Divisibility, by H. E. Newman. The Purification of River Water by Means of Caustic Alkalies, by Alfred Springer. Method for the Assay of Drugs, by H. M. Gordin. Things Unscientific, by Alfred Springer.

APRIL.

MAY.

Proceedings.

COUNCIL.

Abbott, George A., M. T. High School, Indianapolis, Ind.
Aldrich, Thomas B., 284 Pennsylvania Ave., Detroit, Mich.
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Bacon, Raymon F., Vincennes Univ., Vincennes, Ind.
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Cady, Hamilton P., Lawrence, Kansas.
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Ferris, Wm. S., 224 Murray St., Madison, Wis.
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Gillinder, James, Jr., 1509 Oxford St., Philadelphia, Pa.
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Hall, Roy D., 712 Langdon St., Madison, Wis.
Hantke, Ernst, 646 Broadway, Milwaukee, Wis.
Harris, Harry B., Southern Cotton Oil Co., Savannah, Ga.
Hart, Walter H., 2010 Wallace St., Philadelphia, Pa.
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Hendrixson, W. S., Iowa College, Grinnell, Iowa.
Holbrook, George M., 64th St. and Lexington Ave., Chicago, Ill
Hunt, Caroline L., 1566 Ashland Ave., Evanston, Ill.
Isakovics, Alois von, 457 E. 121st St., N. Y. City.
Kern, Edward F., 77 Lenox Ave., N. Y. City.
Kohl, Herbert C., Craigsville, Va.
Little, C. A., Box 517, Elyria, Ohio.
Mains, Elmer E., 415 Humboldt Ave., Detroit, Mich.
McCarthy, Maurice L., 1168 Massachusetts Ave., Cambridge, Mass.
McDonnell, Curtis C., Clemson College, S. C.
McFarland, David F., Univ. of Kansas, Lawrence, Kansas.
Merzbacher, Aaron, Carpenter Steel Co., Reading, Pa.
Montgomery, John P., Starkville, Miss.
Moore, Charles J., Charlottesville, Va.
Moore, Richard B., Univ. of Missouri, Columbia, Mo.
Morre, G. J., Jr., 271 W. 22nd St., N. Y. City.
Mosher, Willet H., Univ. of Buffalo, Chem. Lab., Buffalo, N. Y.
Page, Logan W., 2019 O St., Washington, D. C.
Pray, Charles P., Hempstead, N. Y.
Porter, John L., Water Purification Sta., New Orleans, La.
Price, T. M., College Park, Md.
Ryland, Garnett, Orono, Me.
Schlisinger, Bart E., Warren St., Brookline, Mass.
Smith, Alexander, Univ. of Chicago, Chicago, Ill.
Smith, Edward S., Grasselli Chem. Co., East Chicago, Ind.
Smith, S. M., Elon College, N. C.
Thomas, Geo. E., 1513 N. Gratz St., Philadelphia, Pa.
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Walters, Edward P., 22 Everett Ave., Dorchester, Mass.
Walworth, Joseph E., Lawrence, Mass.
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Wilkins, Albert D., 8 Sprague Ave., Bellevue P. O. Station, Allegheny, Pa.
Wills, J. Lainson, 133 Midwood St., Flatbush, Brooklyn, N. Y.
Wright, Frank, 2421 Dearborn St., Chicago, Ill.
Young, J. Bertrand, 532 Franklin St., Reading, Pa.
Youtz, L. A., 1272 Amsterdam Ave., N. Y. City.
Ziegler, Howard, 526 Penn St., Reading, Pa.
Zeiss, William, 54 Lawrence Ave., Detroit, Mich.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Baldwin, Wareham S., 522 Monroe St., Ann Arbor, Mich.
Bloom, Warren E., 44 Montgomery St., Jersey City, N. J.

Driscoll, J., 71 Centre St., Roxbury, Mass.
Ellett, T. S , 3767 Ellis Ave., Chicago, Ill.
Langmuir, Irving, 185 W. 135th St., N. Y. City.
Law, Leroy M., 310 Ninth St., N. E., Washington, D. C.
McKnight, J. Renwick, Care Wm. Cramp and Sons, York and
Thompson Sts., Philadelphia, Pa.
Sammet, George V., 73 Sheridan St., Boston, Mass.
Sheiry, Dillon, 132 F St., N. E., Washington, D. C.
Smith, Roger G., 314 A St., N. E., Washington, D. C.

MEMBERS ELECTED DECEMBER 27, 1900.

Boesch, Basil W., 36 Union Park, Boston, Mass.
Brown, C. Arthur, 630 W. 8th St., Cincinnati, O.
Burtt, Stratford, 840 Halsey St., Brooklyn, N. Y.
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Cathcart, Wm. R., Maywood, N. J.
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Cook, Alfred N., Sioux City, Iowa.
Davis, Leon K., 185 Temple St., Boston, Mass.
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Kingman, Wm. A., 55 Lincoln St., So. Framingham, Mass.
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Mead, George H., Cellulose Products Co., Boston, Mass.
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Owens, Wm. G., Bucknell Lab., Lewisburg, Pa.
Patterson, G. W., Indian Head, Md.
Roberts, Alfred E., 23 St. Botolph St., Boston, Mass.
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N. Y.
Stieglitz, Julius, Univ. of Chicago, Chicago, Ill.
Tingle, Alfred, Chem. Lab., Columbia University, N. Y. City.
Tingle, John B., Lewis Institute, Chicago.
Tolman, Lucius M., 1937 13th St., N. W., Washington, D. C.
Trowbridge, Dic Hector, Lewis Institute, Chicago, Ill.
Ulmer, George F., Arbuckle Bros., Sugar Ref., Foot of Pearl
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Waterhouse, James S., Cumberland Univ., Lebanon, Tenn
Waters, Charles D., 6 Magnolia St., Roxbury, Mass.
Waters, C. E., Conn. Agr. Coll., Storrs, Conn.
Wesener, John A., Columbus Food Lab., 103 State St., Chicago,
Ill.

ASSOCIATES ELECTED DECEMBER 27, 1900.

Bernheim, George B., 74 E. 79th St., N. Y. City.
Hildreth, Thomas F., 530 W. 123rd St., N. Y. City.
Falk, Kaufman G., 63 E. 74th St., N. Y. City.
Lindsay, Wm. G., 207 W. 81st St., N. Y. City.
Moffatt, Miles R., Mamaroneck, Westchester Co., N. Y.
Page, Robert W., 527 Third St., Brooklyn, N. Y.
Pickhardt, W. Paul, 1042 Madison Ave., N. Y. City.

CHANGES OF ADDRESS.

Arnott, G. W. Campbell, 4 Cedar St., N. Y. City.
Atkinson, J. W., Betteravia, Cal.
Baekeland, Leo, "Snug Rock," Harmony Park, Yonkers,
N. Y.
Barrett, Jesse M., 618 Packard St., Kansas City, Kansas.
Bassett, Geo. O., American Bell Tel. Co., 125 Milk St., Boston,
Mass.
Becher, Jesse B., 1120 Douglass St., Sioux City, Iowa.
Benson, D. H., Box 475, Pictou, N. S.
Boltwood, Bertram B., 139 Orange St., New Haven. Conn.
Brinton, C. S., Box 16, West Chester, Pa.
Broadhurst, W. Homer, 13–21 Park Row, N. Y. City.
Calvert, Joseph E., Blairsville, Pa.
Cook, Charles G., 815 Marcy Ave., Brooklyn, N. Y.
Closson, C. D., Phoenix Mines, Cave Creek, Ariz., *via* Phoenix,
Ariz.
Culmann, Julius, 843 Front Ave., Buffalo, N. Y.
Darke, J. M., 103 Shepard St., Lynn, Mass.
Doolittle, O. S., 445 Oley St., Reading, Pa.
Dorr, J. V. N., Florence, Colo.
Enright, Bernard, "The Broadway," South Bethlehem, Pa.
Evans, James A., 57 Burt St., Cleveland, O.
Evans, Wm. L., Box 1461, Colorado Springs, Colo.
Fischer, Robert, Ithaca, N. Y.
Frost, H. V., 3958 Drexel Boulevard, Chicago, Ill.
Fullam, Frank L., Care Int. Sm. Powder and Dynamite Co.,
South Amboy, N. J.
Gerlach, Oscar, Iola Portland Cement Co., Iola, Kans.
Given, Arthur, Glasgo, Conn.

Hancock, W. J., Erasmus Hall High School, Brooklyn, N. Y.

Hanna, D. C., 4262 Parkside Ave., Phila., Pa.

Hayes-Campbell, J., Rockwood Hotel, Rockwood, Tenn.

Herrick, Rufus F., 16 Herrick St., Winchester, Mass.

Hinds, J. I. D., Univ. of Nashville, Nashville, Tenn.

Irwin, Edward P., 7010 Princeton Ave., Chicago, Ill.

Jones, A. B., Versailles, Allegheny Co., Pa.

Kendall, Arthur I., 1409 Calhoun St., New Orleans, La.

Kert, W. H., 292 Clifton Place, Brooklyn, N. Y.

Knight, G. W., 38 Rosseter St., Boston, Mass.

Lagai, G., 225–233 Fourth Ave., N. Y. City.

Langmuir, A. C., Care Marx and Rawolle, 9 Van Brunt St., Brooklyn, N. Y.

Linton, J. H., care Tenn. C. I. & R. Co., Ensley, Ala.

Lockwood, Rhodes G., 118 Beacon St., Boston, Mass.

Maas, Philip, Central High School, Phila., Pa.

Maywald, F. J., 1028 72nd St., Brooklyn, N. Y.

Miller, Hugh L., care Va.-Ca. Chem. Co., Columbia, S. C.

Norman, Geo. M., 1035 Elizabeth Ave., Elizabeth, N. J.

Norris, R. S., Betteravia, Cal.

McDowell, Alex. H., Grand Junction, Mesa Co., Colo.

Miles, G. W., Jr., 29 Central St., Boston, Mass.

Miller, S. C., 929 N. Y. Ave., N. W., Washington, D. C.

Miller, W. Lash, 50 St. Alban St., Toronto, Can.

Moore; Geo. D., 201 Salisbury St., Worcester, Mass

Murrill, Paul I., Auburn, Ala.

Post, Frank I., 142 Morse St., Coldwater, Mich.

Redding, Allen C., Baker City, Ore.

Richards, Theo. W., 15 Follen St., Cambridge, Mass.

Rising, Herbert R., 208 Water St., Johnstown, Pa.

Ritchey, J. C., Lake Superior Copper Co., Sault Ste. Marie, Ont.

Saunders, A. P., Hamilton College, Clinton, N. Y.

Schoonmaker, H., 917 Race St., Cincinnati, O.

Scudder, Heyward, " The Ludlow," Boston, Mass.

Shilstone, Herbert M., Care Julian H. Archer & Co., 458 Produce Exchange, N. Y. City.

Skinner, Hervey J., 11th and Linden Sts., Camden, N. J.

Sohon, M. D., 3080 Third Ave., N. Y. City.

Stevens, Edward K., 8 Washington Sq., Newport, R. I.

Sullivan, E. C., 1218 So. University Ave., Ann Arbor, Mich.

Summey, A. E., Athol Springs, N. Y.

Watson, E. F., 269 S. Third St., Columbus, Ohio.

Wesson, David, Box 458, Savannah, Ga.

White, Alfred H., 626 Forest Ave., Ann Arbor, Mich.

White, C. H., Center Sandwich, N. H.

White, Laura B., Wallingford Road, Boston, Mass.
Wiechmann, F. J., Box 79, Station W, Brooklyn, N. Y.
Willard, H. H., 520 E. Ann St., Ann Arbor, Mich.
Wilson, Herman T., Archer Starch Co., Bradley, Ill.
Witherspoon, T. M., Examiner, U. S. Patent Office, Washington, D. C.
Wolfe, J. V., Jr., Lincoln, Nebr.

ADDRESSES WANTED.

Poole, Hermann, formerly of 357 Canal St., N. Y. City.
Youmans, W. J., formerly of 72 5th Ave., N. Y. City.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The thirteenth meeting was called to order in the John Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., September 13, 1900, Dr. Jayne in the chair. Twenty-eight (28) members and visitors were present.

Minutes of the last meeting were read and approved.

It was moved and seconded that a committee of five be appointed to consider the Brosius Bill, which has been brought before the section. Carried.

It was moved and seconded that the chair appoint the committee. Carried. Messrs. Leffman, Kebler, Remington, Keller, and Schlichting were appointed.

The paper of the evening was "The Rapid Determination of Carbon in Steel," by Mr. Robert Job.

The paper was discussed by Messrs. Sargent, Jayne, and Auchy.

There being no further business, the meeting adjourned at 9.45 P.M.   F. E. DODGE, *Secretary.*

NEW YORK SECTION.

The regular meeting of the New York Section of the American Chemical Society was held on the evening of December 7, 1900, at the Chemists' Club, 108 West 55th Street, Dr. C. A. Doremus presiding.

Special invitations had been sent out to those interested in public water supply, as the feature of the meeting was an address by Professor William P. Mason, of the Rensselaer Polytechnic Institute, of Troy, entitled "The Water Supplies of the Cities on the Mediterranean," with lantern illustrations.

The address, which was fully illustrated by lantern slides from photographs taken while on his trip, began with a description of Gibraltar, and its peculiar arrangements for water supply. From there to Tunis and other cities on the south shore, including the site of ancient Carthage ; then to Naples and Rome.

The system at Naples, once so primitive and unsanitary, is now on a scale and of a character to command admiration.

The typhoid epidemic at Hamburg in 1892 was alluded to, and a " spot" map, showing the number of cases by black spots, gave a graphic representation of the severity of the scourge in Hamburg, and the comparative immunity of the adjoining town of Altona, which, while having a separate water supply, was not more separated from Hamburg than Harlem from the rest of New York City.

At the close of the address a vote of thanks was passed, and some routine business attended to. Four representatives in the council were elected, and a committee of three was appointed to confer with the Bureau of Combustibles in regard to the present existing restrictions as to storage of nitric, hydrochloric, and sulphuric acids.

Messrs. T. J. Parker, A. P. Hallock, and William McMurtrie were appointed on this committee.

The situation, as it now stands, is such that a permit can be obtained for 1,000 pounds only of the acids named, whereas many establishments are using more than this amount every twenty-four hours, and, aside from the difficulty of having the acids delivered each day, any interference with daily delivery would result in suspension of large and important industries.

The stated meeting was held January 11, 1901, at the Chemists' Club, 108 West 55th Street, as usual. Dr. C. A. Doremus presided, and 53 members were present.

The minutes of the December meeting were read and accepted. The November minutes were read and accepted.

Dr. Parker reported progress for the committee appointed to confer with the Bureau of Combustibles in regard to the storage of acids.

The chair reported that the revision of the by-laws was in the hands of the Executive Committee in accordance with the action

taken at the November meeting. A resolution offered by A. C. Hale, was then read as follows :

" *Resolved*, That the New York Section of the American Chemical Society herewith extends a most cordial invitation to the Society to celebrate the twenty-fifth anniversary of its foundation next April in New York City, and the chairman of the New York Section is hereby authorized and directed to appoint such local committees as he may deem expedient in order to aid in perfecting arrangements for such celebration."

The resolution was unanimously approved and the Secretary was instructed to instruct Secretary Hale to formally extend the invitation to the Society at large.

Dr. T. O'Connor Sloane then read his paper entitled "Notes on Spheroidal State Evaporation," with experiments.

Dr. McMurtrie made a report on the mid-winter meeting just held in Chicago, to the effect that it had been very successful, and the visiting members were well entertained. One hundred and thirty-nine members were registered. Numerous applications for membership in the Society had been entered as a result of the interest aroused.

No further business coming before the meeting, adjournment was then taken. DURAND WOODMAN, *Secretary.*

WASHINGTON SECTION.

A regular meeting was held October 11, 1900. The evening was devoted to the address of the retiring president, Dr. H. N. Stokes, on the subject " The Revival of Organic Chemistry."

A regular meeting was held November 8, 1900.

The first paper of the evening was read by Mr. L. M. Tolman, and was entitled " The Examination of Jellies, Jams, and Marmalades," by L. M. Tolman, L. S. Munson, and W. D. Bigelow.

The paper gave the results of the examination of jellies and jams manufactured in the laboratory from thirteen varieties of fruits. The solids, ash, acid, nitrogen, reducing sugar and cane-sugar, were determined, and the amount of cane-sugar inverted was calculated.

The juices and pulps from which the samples were made were also examined. The relation between the acid content and the content of cane-sugar inverted was especially noted.

The second paper of the evening was read by Dr. Bigelow and

was entitled " The Nitrogenous Compounds of Meat Extracts," by W. D. Bigelow and R. Harcourt.

The authors examined about fifty commercial extracts making use of the following methods :

Precipitation by bromine as directed by Allen ; precipitation by zinc sulphate ; precipitation by ammonium sulphate ; precipitation by bromine in filtrate from the zinc sulphate precipitate ; precipitation by tannin and phosphotungstic acid (filtered separately), the latter precipitate being filtered at about 90° C., as directed by Mallet.

The bromine precipitate from the original solution was found to hold only a small and variable portion of the proteids present. The zinc sulphate precipitate plus the bromine precipitate in the filtrate from the same gave results which were fairly satisfactory. The best results were obtained by the use of Mallet's method. Mixtures of digested egg albumen and purified meat bases were also subjected to the above methods.

The regular meeting was held on December 13, 1900.

The first paper of the evening was entitled " The Composition of the Ash of Meat Extracts," by W. D. Bigelow and E. McK. Chace.

The relations between solids and ash and between the several ash constituents were discussed in analyses of about forty commercial meat extracts and of juices prepared from fresh beef.

The second paper was read by Dr. Cameron and was entitled " Formation of Sodium Carbonate or Black Alkali by Plants."

The view popularly held to which Hilgard, Goss, and others have called attention, is found to be correct. It seems probable that the phenomenon is very wide-spread, but does not assume practical importance, except under special conditions in the arid regions. A discussion of the rôle of mineral nutrients in soil solutions accompanied the consideration of the data experimentally determined.

The last paper was read by Dr. Cameron and was entitled " Resistance by Certain Plants to Black Alkali."

It has been found that a few plant species exist which can grow in soils containing much sodium carbonate. Three such plants were examined. It was found that these plants had an organic

acid or acids formed on their surface, sufficiently strong to decompose alkaline carbonates. It is believed that this acid or acids aid in lowering the concentration of the alkaline carbonates in the soil immediately about the plants and thus protect the root crowns from the caustic action of the black alkali.

<div align="right">WILLIAM H. KRUG, Secretary.</div>

CHICAGO SECTION.

The thirty-seventh regular meeting of the Chicago Section was held January 16, 1901.

A very interesting paper, followed by a discussion, was given by Dr. R. A. Millikan, of the Department of Physics, of the University of Chicago.

The Section elected the following officers for the year 1901: President, Felix Lengfeld ; Vice-President, Gustav Thurnaur ; Secretary, F. B. Dains ; Treasurer, C. W. Patterson ; Executive Committee, Felix Lengfeld, F. B. Dains, and Edw. Gudeman.

<div align="right">F. B. DAINS, Secretary.</div>

NOTICE.

Letters have been received from prominent chemists in Washington and elsewhere, warning chemists and chemical firms against a man who claims to be a deaf mute. His record has been traced in part, and he is pronounced by those in a position to know to be a rank impostor. In Washington he claimed to be a Ph. D. of Vienna, and gave a spurious reference. In Baltimore he gave a different reference. He is described as thick set, about five feet six inches to five feet eight inches tall, with rather flat face and pointed chin, smooth shaven, except for a small dark mustache curled up at the ends, and wearing a gold seal ring on left hand. He is not the person referred to in a former cautionary notice.

ALBERT C. HALE,
<div align="right">Secretary American Chemical Society.</div>

Proceedings.

MINUTES OF THE TWENTY-SECOND GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The first session of the Twenty-Second General Meeting of the American Chemical Society was held in Lewis Institute, Chicago, Ill., Thursday, Dec. 27, 1900. The session was called to order by President McMurtrie, in the Chemical Lecture Room of the Institute, at 10.15 A.M. Dr. W. R. Smith, chairman of the Chicago Section of the Society, was introduced and welcomed the chemists in behalf of the local section. He was followed by Howard S. Taylor, Esq., prosecuting attorney for the city of Chicago, who addressed a few words of welcome in behalf of the city and its citizens. President McMurtrie responded briefly in behalf of the Society, thanking the speakers for their cordial words of welcome.

After a few announcements, a paper on "Correction in the Determination of Urea by the Liebig Method" was read by J. H. Long. This was followed by another paper by the same author on "Preliminary Note on the Optical Rotation of Certain Tartrates in Glycerol." The latter paper was discussed by Messrs. W. A. Noyes and Long.

A paper on "The Decomposition of Sodium Nitrate by Sulphuric Acid, Part II," by C. W. Volney, was read by the author.

Edward Gudeman presented a brief paper on "Arsenical Poisoning," which was discussed by Messrs. Springer, Volney, and Gudeman, and Miss Fossler.

Two papers by C. L. Parsons entitled "A Simple Test for Distinguishing Oleomargarine from Butter," and "The Use of Metallic Sodium in Blowpipe Analysis" were read by the secretary in the absence of the author.

A photograph of the assembled chemists was taken, and after a few announcements, the morning session was adjourned.

At the close of the morning session luncheon was served in the building, through the courtesy of the authorities of the Lewis Institute.

The Council of the Society met at the Lewis Institute at 1.30 P.M. Other members of the Society participated in visits to the works of Messrs. Frazer and Chalmers, the Consumers Ice Company, and the Eisendraht Tannery of the American Hide and Leather Co.

The evening session of the Society was held in the Banquet. Hall of the Auditorium Hotel, Dr. W. R. Smith, vice-president of the Society and chairman of the Chicago Section, presiding.

The retiring president, Dr. Wm. McMurtrie, delivered an address on "The Condition, Prospects, and Future Educational Requirements of the Chemical Industries."

After a few announcements the session adjourned. A brief session of the Council was held at 9 P.M., and later the visiting chemists enjoyed a "smoker," given by the members of the local section, at the Technical Club, 230 South Clark Street.

FRIDAY, DECEMBER 28TH.

The session on Friday was held in the Chemical Lecture Room of the Northwestern University Medical and Pharmacy School, 2421 Dearborn Street.

The meeting was called to order by President McMurtrie at 9.30 A.M.

The annual reports of the secretary, the treasurer, and the librarian were presented in order and read by the secretary. These reports were accepted by the Society and ordered placed on file.

President McMurtrie made a few remarks regarding the thorough work which had been accomplished by the librarian during the past year, and on motion of Dr. Hart the thanks of the Society were voted to the librarian for his successful and faithful services.

The editor presented a brief oral report of his work.

Reports received by the secretary from F. W. Clarke, chairman of the Committee on Atomic Weights, and also chairman of the

International Committee on Atomic Weights, were presented by the secretary, in the absence of Mr. Clarke and were read by title and referred to the Committee on Papers and Publications.

The secretary reported from the Council that that body had considered the question referred to it by the Society at the New York Meeting with reference to the passage of H. R. Bill 104, looking to the adoption and use of the metric system and had decided to recommend that the Society lay the question on the table. By a vote of the Society the recommendation of the Council was adopted and the question was laid on the table.

The Committee on Standards for Instruments of Measure reported progress through Messrs. Munroe and Linebarger, who urged immediate action on the part of the membership with reference to the bill now pending in Congress to establish a National Standards Bureau.

The secretary presented a motion offered by Mr. Albert P. Sy, urging the appointment of a committee to consider the adoption of a permanent badge or pin by the Society. The motion being seconded, it was moved and carried that the whole matter be laid upon the table.

The president announced that F. W. Clarke, of Washington, D. C., had been elected president of the Society for the year 1901, and that the following named members had been elected councilors to serve three years, beginning January 1, 1901 : William A. Noyes, F. A. Gooch, T. W. Richards, and H. L. Wells.

After some other announcements W. A. Noyes presented a paper on " Synthesis of Derivatives of Dimethyl-cyclopentanone and of β-β-Adipic Acid, and of α-β-β-Trimethyladipic Acid." Dr. Noyes also presented a paper by himself and W. M. Blanchard on " A New Hydroxydihydrocampholytic Acid."

After some other announcements, Professor A. B. Prescott presented a paper by P. F. Trowbridge entitled "Notes on Sugar-Beet Analysis." This was followed by a paper " On Haematite Crystals," by Charles E. Munroe.

The remaining papers on the program were read by title.

On motion of Dr. Alfred Springer, the thanks of the Society were extended unanimously to the Chicago Local Section ; the Local Committee of Arrangements for the Meeting, the authorities of the various institutions which had extended courtesies to

the Society during their meeting, and the proprietors of the various works which had been thrown open to inspection by the visiting chemists.

The Local Committee made some announcements with reference to a proposed excursion to South Chicago on Saturday morning and the meeting of the Society was then adjourned.

In the afternoon the chemists enjoyed an excursion and visit to the Stock Yards Industries, and at 7 P.M. a subscription dinner was given in the Banquet Hall of the Auditorium Hotel.

ALBERT C. HALE, *Secretary.*

REPORT OF THE SECRETARY.

The annual meeting of the Society was held last year in New Haven, Conn., December 27th and 28th. The meeting was one of unusual interest, and there was a large attendance. The summer meeting was held in New York City during the last week in June, in connection with the meeting of the American Association for the Advancement of Science. It was thought by those who fixed the date so early for the meeting of the Association that, by that means, they would secure the attendance of many who were expecting to go abroad during the summer to visit the Paris Exposition. As a fact, however, a very large proportion of such members took their departure before the date of the meeting, and this affected considerably the attendance, both at the Association gatherings, and at those of the American Chemical Society.

The urgent invitation which was given by the Chicago Section to hold the meeting of the Society in that city in December, 1899, was renewed with additional cordiality for the following year. The Council at the New York Meeting, therefore, voted unanimously to hold the annual meeting of the year 1900 with the Chicago Section, and thanks to the persistent efforts of our friends of that city and section we are now enjoying their bounteous hospitality.

The American Association for the Advancement of Science has decided to hold its meeting next summer in Denver, during the week beginning August 26th, and if our Society should follow its usual custom, its summer meeting will be held in that city, August 26th and 27th. This question will be decided as usual by the Council. Invitations and suggestions for the next two meetings

have also been received in a somewhat informal way, but it is as yet too early to speak definitely regarding them.

At the New York Meeting, the president of the Society was authorized and directed to appoint a committee, of which he himself should be chairman, with power to arrange for the celebration of the 25th anniversary of the foundation of the Society, which will occur April 6, 1901. The committee has been appointed, and the names of the members have been given to the Society in a printed list sent by mail. Subcommittees have already been appointed, and the preliminary arrangements for the anniversary will probably soon be well under way.

The library this year has been under the efficient management of Dr. E. G. Love, and is likely to be much more serviceable to the Society in the future than it has ever yet been. The library had been already well housed and shelved in the rooms of the Chemists' Club, New York, where it is still kept, and Professor Breneman, the acting librarian during the greater portion of the year 1899, had done most excellent service in putting it into good working condition.

During the past year the Committee on Abstracts and Reviews was discharged, and a committee was appointed to report at this meeting, upon the advisability of preparing a title-index of papers for the Journal. President McMurtrie was appointed chairman of this committee, which, as a result of its work, has elaborated a plan embracing the whole question of abstracts, etc.

The Committee on the Frankland Memorial reported at the New Haven Meeting, and that on the Bunsen Memorial at the New York Meeting. A new Committee on Duty-Free Importation was appointed under authority of the Council, last February, with Professor Charles E. Munroe as chairman. In connection with the Journal, there has been appointed a Committee on Portraits, Dr. Marcus Benjamin, chairman ; and a Committee on Paper for the Journal, Dr. Edward Hart, chairman.

At the New York Meeting a resolution was presented, favoring the passage of the H. R. Bill 104, with reference to the Metric System of Weights and Measures. This was referred to the Council to report upon at the present meeting.

Early in the year, the Chemical Publishing Company gave notice of the termination of the contract for publishing the Jour-

nal. This notice was accepted by the directors, who also agreed to a temporary arrangement proposed by the Chemical Publishing Company, pending the formation of a new contract, and the action of the directors was ratified by the Council. By authority of the Council at the New York Meeting, the following persons were appointed as a Committee on a New Contract for the Journal : Wm. McMurtrie, C. B. Dudley, M. L. Griffin, A. D. Little, and H. N. Stokes. The committee will probably present a report to the Council at the present meeting.

In accordance with the action of the Council at the New Haven Meeting, it becomes the duty of the Council at each annual meeting to place in nomination the officers and committees which are to be elected by the Council for the ensuing year. The Council has also to prepare a budget of expenses for the Society for the coming year, based upon an estimate of necessary expenses prepared by a committee consisting of the president, the secretary, the treasurer, and the finance committee.

The directors have adopted a new schedule of rates for back numbers and subscriptions to the Journal during the past year, and this schedule has already been published.

The Society has at present 13 local sections, the Council having authorized the establishment of one in Kansas City and vicinity, November 6th. This section has already been chartered and organized, with 21 members, local officers, and a delegate to the Council.

The following statistics derived mainly from their annual reports, show something of the condition and work of the various sections during the year just closing :

Rhode Island Section.—Present membership, 34 ; gain during the year, 7 ; number of meetings, 9 ; number of papers presented, 7.

Cincinnati Section.—Present membership, 68 ; gain during the year, 1 ; number of meetings, 7 ; number of papers presented, 9.

New York Section.—Present membership, 389 ; gain during the year, 28; number of meetings, 9; number of papers presented, 37.

Washington Section.—Present membership, 109 ; gain during the year, 4 ; number of meetings, 13 ; number of papers presented, 28.

Lehigh Valley Section.—Present membership, 18 ; loss during the year, 1; number of meetings, 1; number of papers presented, 4.

Chicago Section.—Present membership, 65 ; gain during the year, 13 ; number of meetings, 6; number of papers presented, 7.

Nebraska Section.—Present membership, 15 ; loss during the year, 3 ; number of meetings, 4 ; number of papers presented, 8.

North Carolina Section.—Present membership, 22 ; gain during the year, 1; number of meetings, 1; number of papers presented, 6.

Columbus Section.—Present membership, 21 ; loss during the year, 1 ; number of meetings, 8.

North Eastern Section.—Present membership, 237 ; gain during the year, 9 ; number of meetings, 8; number of papers presented, 15.

Philadelphia Section.—Present membership, 107 ; gain during the year, 10 ; number of meetings, 12 ; number of papers presented, 16.

Michigan Section.—Present membership, 48 ; number of meetings, 2.   This section held its first meeting in February of this year.

Kansas City Section.—Present membership, 21.   This section has just been chartered, November 6, 1900.

The membership of the Society has increased during the past year from 1569 to 1715, the changes in membership being as follows :

New members added during 1900 ···		234
Resigned	44	
Dropped for non-payment of dues···	41	
Died	3	
Total loss................... ——		88
Net gain for the year.........		146

The Society has lost by death the following named members : N. P. Hill, of Colorado ; Edward R. Squibb, of Brooklyn ; and Allan Wells, of Pittsburg.

The total number enrolled in the various local sections is 1154; other members, 561. The per cent. in local sections is 67+, being almost identical with that of last year.

Two new honorary members, Edward W. Morley, of Cleve-

land, Ohio, and Wilhelm Ostwald, of Leipzig, Germany, have been elected during the year, to fill the places of Professors Frankland and Bunsen, who died in 1899.

The increase of membership during the past year has been about the same as the average annual increase since the year 1890, when the Society inaugurated its present plan of establishing local sections, and holding two general meetings in different localities annually. Under the inspiration of the coming 25th anniversary of the Society, it is hoped that the membership will reach the round number of 2,000 before the date of that meeting. The following appeal which has already been mailed to the members in connection with the announcement regarding the anniversary may well be repeated here. " It is hoped that all will unite in an effort to make this occasion the most memorable one in the annals of our Society, one which shall mark an epoch in its development and progress, shall record its history and achievements, shall show the representative character and strength of this organization of American chemists, and shall point the way to higher attainments and greater triumphs in all departments of pure and applied chemistry in the new world.

" The Society has now over 1700 members upon its roll, and it is believed that with suitable effort upon the part of its present membership the number could be brought up to 2,000 before the date of its 25th anniversary. We earnestly solicit your most hearty cooperation to this end, and trust that you will aid in this effort by nominating to membership or associate membership some personal acquaintance who is interested in the science of chemistry."

<div align="center">Respectfully submitted,</div>

<div align="right">ALBERT C. HALE, <i>Secretary.</i></div>

<div align="center">REPORT OF THE TREASURER FROM DECEMBER 21, 1899 TO DECEMBER 21, 1900.</div>

<div align="center">NEW YORK, N. Y., December 21, 1900.</div>

<div align="center">RECEIPTS.</div>

Balance in Knickerbocker Trust Co., Dec. 21, 1899			$ 332 39
Received from dues			7,500 00
"	"	back numbers	322 98
"	"	subscriptions	917 29
"	"	advertising	1129 50

Received from A. A. Breneman, library............... $ 30 30
    "   "   Philadelphia Section returned 67 00
    "   "   Cincinnati   "   " 2 25
    "   "   interest Knickerbocker Trust Co.......   16 55
    "   "   "   special investment fund.......   70 00
    "   "   life-membership, C. B. Dudley......... 100 00
    "   "   interest life-membership fund..........   35 00
                                     —————$10,190 87

                                        $10,523 26

DISBURSEMENTS.

For printing Journals................................ 3206 72
Authors' reprints.................................... 214 68
Expense president's office........................... 40 58
    "   editor's   " 111 21
    "   secretary's " (clerical)................... 625 66
    "   "   " (current)................... 145 37
    "   "   " (general)................... 419 96
    "   "   " collection of dues 750 00
    "   treasurer's " 28 03
    "   librarian's " 265 05
    "   library (binding and completing files) 180 52
    "   "   (clerical help)...................... 35 00
    "   "   furniture........................... 74 38
    "   advertising 21 00
    "   back numbers, storage, etc................... 18 95
    "   printing directories 184 00
    "   Review of American Chemical Research...... 48 90
    "   Standards Bureau 9 81
    "   editor's salary 1899–1900 .... 500 00
    "   treasurer's salary 1899–1900 .... 350 00
    "   rebate on subscriptions 20 00
    "   New Haven Meeting........................ 59 48
    "   New York Meeting......................... 71 00
    "   Chicago Meeting 36 75
    "   incidentals................................. 118 74

                                         $7535 79

    "   local sections, *viz :*

                Chicago .... $ 80 00
                Cincinnati 86 66
                Columbus.................... 26 66
                Lehigh Valley 21 66
                Michigan 48 33
                Nebraska 25 00
                New York 400 00
                North Carolina.............. 21 66

North Eastern	$313 33	
Philadelphia	50 00	
Rhode Island	25 00	
Washington	86 66	
		$1184 96

$8720 75

Paid loan Knickerbocker Trust Co	$1200 00	
Interest on loan	23 20	
		1223 20
Deposit Emigrants' Savings Bank	$135 00	
Balance in Knickerbocker Trust Co., and on hand	444 31	
		579 31
		$10,523 26

ASSETS.

Special investment fund ($2000, 3½ per cent. N. Y. gold bond due 1915)		$2097 50
Life-membership fund ($1000, 3½ per cent. N. Y. gold bond, due 1925)	$1080 38	
Emigrants' Savings Bank	219 62	
" " " from C. B. Dudley	100 00	
		1400 00
Balance in Knickerbocker Trust Co		410 46
Cash in treasurer's hands		33 85
" " secretary's "		287 90
". " librarian's "		35 07
Uncollected accounts, librarian's office		117 33
" " advertising		1188 80
" " dues for 1899	$335 00	
" " " " 1900	945 00	
		1280 00
		$6850 91

LIABILITIES.

Life-membership fund		$1400 00
Unexpended library appropriations		295 10
		$1695 10
Balance of actual assets		5155 81
		$6850 91

A. P. HALLOCK, *Treasurer.*

Accounts examined and found correct, E. & O. E.

J. H. WAINWRIGHT,
ELWYN WALLER.

REPORT OF THE LIBRARIAN.

Number of copies of the Proceedings and the Journal on hand :

In storage warehouse	36,470
At Chemists' Club	11,892
Total	48,362

Number of copies sent out by the librarian from February 5th to date, 3,195.

As nearly as can be determined these were distributed as follows :

As " back numbers " to members and subscribers	2,231
Sold	919
To replace copies lost in mail	37
" " imperfect copies	8
Total	3,195
Amount received from sales of the Proceedings and the Journal to December 15th, and transmitted to the treasurer	$322.98
Uncollected accounts	117.33

The expenses of the librarian's office from February 5, to December 1, 1900, have been as follows :

Postage	$61.69
Stationery and printing	43.13
Library supplies	10.15
Express and incidentals	30.81
Total	$145.78

Appropriation of $400 for completing files and for binding.

Number of volumes bound	118
Cost	$162.40

The balance of this appropriation has been expended or contracted for in completing the files of journals in the library. Several orders which were placed with European book dealers some time ago have not been filled at this date, but upon the receipt of the material ordered the following files will have been completed, or nearly completed, under this appropriation :

American Chemical Journal, completed.
Journal of the Society of Chemical Industry, nearly completed.
Journal of the Chemical Society, nearly completed from 1877.
Chemical News, nearly completed.

Zeitschrift für angewandte Chemie, completed.
Analyst, completed.
Archiv du Pharmacie, completed from Vol. 17.
Zeitschrift für analytische Chemie, completed.
Pharmaceutical Journal, completed.
Transactions Institute Electrical Engineers, partially completed.
Journal of Physical Chemistry, completed by donation.

These additions amount to about 308 volumes and 329 single numbers. The aim has been to complete the more important files first ; but in one or two instances it has seemed advisable to accept advantageous offers of material which was necessary to complete other files of not so much importance.

A complete list has been made of all the material in the library, and a card catalogue is in course of preparation.

Donations to the library have been received from the following:
F. P. Venable, E. H. Miller, Geo. C. Arnott, G. H. Boggs, E. P. Howe, E. F. Hicks, E. N. Pattee, H. Schweitzer, editors of *Journal of Physical Chemistry*, and Blakiston's Son and Co.

E. G. Love, *Librarian*.

REPORT OF THE COMMITTEE ON DUTY-FREE IMPORTATIONS.

To the Council of the American Chemical Society.

GENTLEMEN : Your committee begs leave to report that as the effect of the tariff legislation secured in the last Tariff Act is very greatly modified by the rulings of the Treasury Department, it has deemed it essential to make a study of tariff legislation as shown in the various Acts of Congress and of the rulings of the Treasury Department and hereby submits the record as found in the following report. The first tariff act was passed in the first session of the first Congress on July 4, 1789. The second Tariff Act passed by the first Congress at its second session on August 10, 1790, specifically excepted from duty " philosophical apparatus, specially imported for any seminary of learning."

The Tariff Act of April 27, 1816 extended this provision by declaring " That the following articles shall be imported into the United States, free of duties : ...... philosophical apparatus, instruments, books, maps, charts, statues, busts, casts, paintings, drawings, engravings, specimens of sculpture, cabinets of coins, gems, medals, and all other collections of antiquities, statuary,

modeling, painting, drawing, etching or engraving, specially imported by order and for use of any society, incorporated for philosophical or literary purposes, or for the encouragement of the fine arts, or by order, and for the use of any seminary of learning, specimens in natural history, mineralogy, botany, and anatomical preparations, models of machinery, and other inventions, plants and trees.''

This exemption was again declared in the Tariff Acts of September 11, 1841, and August 30, 1842, the phraseology being changed in the latter to read as follows :

'' Philosophical apparatus, instruments, books, maps, and charts, statues, stationery, busts and casts of marble, bronze, alabaster, or plaster of Paris, paintings, drawings, engravings, etchings, specimens of sculpture, cabinets of coins, medals, gems, and all other collections of antiquities, provided the same be especially imported in good faith for the use of any society incorporated or established for philosophical or literary purposes, or for the encouragement of the fine arts, or for the use and by the order of any college, academy, school or seminary of learning in the United States.''

Although all the other articles mentioned in the foregoing clause appear on the free list, apparently by an inadvertence, philosophical instruments and apparatus are not enumerated among the articles exempt from duty in the Tariff Act of July 30, 1846, or in the Acts of the succeeding Congresses up to March 3, 1857, when the phraseology of the Act of August 30, 1842, is repeated. This Act prevailed until a new one was enacted on March 2, 1861, which, while making many sweeping changes, retained the same phraseology and provisions as to philosophical instruments, etc. The necessities of the Civil War, however, compelled the authorities to seek revenue from every possible source and in the Act of June 30, 1864, it was enacted '' That so much of ...... the Act ...... approved March 2, 1861, as exempts from duty all philosophical apparatus and instruments imported for the use of any society incorporated for philosophical, literary, or religious purposes, or for the encouragement of the fine arts, or for the use or by the order of any college, academy, school or seminary of learning in the United States is hereby repealed and the same shall be subject to a duty of 15 per centum *ad valorem.*''

By the Tariff Act of July 14, 1870, apparatus was restored to the free list in the following terms :

" Philosophical and scientific apparatus, instruments, and preparations ...... specially imported in good faith, for the use of any society or institution incorporated or established for philosophical, educational, scientific or literary purposes, or encouragement of the fine arts, and not intended for sale."

This phraseology was repeated in the Acts of March 3, 1883, and October 1, 1890, except that the word 'religious' was inserted before philosophical in enumerating the kind of societies or institutions, and as thus modified it was repeated in the Act of August 27, 1894, except that the opening declaration was amended to read " Philosophical and scientific apparatus, utensils, instruments, and preparations, including bottles and boxes, containing the same," etc., etc.

Finally, in the Tariff Act of July 24, 1897, the declaration of articles exempt from duty under Section 638 took the following form : " Philosophical and scientific apparatus, utensils, instruments, and preparations, including bottles and boxes containing the same, specially imported in good faith, for the use and by order of any society or institution incorporated or established solely for religious, philosophical, educational, scientific, or literary purposes, or for the encouragement of the fine arts, or for the use or by order of any college, academy, school, or seminary of learning in the United States, or any State or Public Library, and not for sale, subject to such regulations as the secretary of the treasury shall prescribe " and this is existing law.

This history shows that beginning with the first Congress and extending to the present, except by inadvertence in framing the Free Trade Act of 1846 and during the period while the burdens of the Civil War lay heavy upon the country, it has been the endeavor of our national legislators to exempt from duty the tools of instruction and they have been logical in this since it was recognized from the founding of the colonies that the education of the masses is essential to the existence of a free government and taxes have been freely laid for its maintenance. Nevertheless the evident purpose of Congress has been repeatedly thwarted by the revenue officials who have sought to make rulings which would subject the tools and materials used in education to duty.

This is shown in the following letters received by your committee as first appointed :

DEAR MR. MUNROE :

I have received your circular and write to say that I know more about the phrase " philosophical or scientific instruments and preparations " than any one still in active life. I chanced to be in Washington, delivering a course of lectures at the Smithsonian, in January, 1870, when the tariff was under discussion. My late friend Mr. Hooper was Chairman of the Ways and Means Committee, and at his instance I was consulted as to the phraseology and incompatibles in the schedule of drugs and chemicals. Up to that time " Philosophical Instruments " alone had been placed on the free list, and this term was interpreted to cover only brass instruments such as are found in collections of physical apparatus. As I was given the opportunity I urged that all materials whatsoever used for teaching or scientific investigation should be put on the free list, but I learned through Mr. Hooper that the committee feared such a sweeping provision, because it would open the door to evasion ; and the phrase quoted above was the result of numerous consultations. " Scientific instruments and preparations " was intended to cover all such material imported *bona fide* for an educational institution such as glass- and porcelain-ware used in chemical laboratories and also chemicals. I objected to the phrase on the ground that such an interpretation could be easily set aside by the collectors of ·the several ports, but Mr. Hooper said he would attend to that. In fact the first importations I made after the bill was enacted were challenged both at Boston and New York. I appealed as directed, and wrote to Mr. Hooper, and, as he had promised, the appeal was granted. Thus the free entry of chemical goods ever since rests on this decision, although I am told that the New York and Philadelphia collectors have attempted to override the decision this last year. I have felt that it was unwise to meddle with the old arrangement, although of course I would prefer a more liberal policy; but there is great danger of losing what we have secured if we stir the mud. I don't believe in your rebate proposition. It would complicate matters immensely and increase the cost of importations. If I was going in for a change I would prefer the proposition of the

National Academy, adding however "for the sole purpose of teaching." Remember I have been in the business forty-five years.

<div align="right">Very truly,</div>

(Signed)   JOSIAH P. COOKE.

<div align="right">CAMBRIDGE, January 28, '94.</div>

DEAR Mr. MUNROE :

I have your answer to my letter called forth by your circular. Since writing that letter I have been visited by an agent of one of the large firms who as you say are moving in the matter and I told him what substantially I wrote to you. The immediate motive of the movement is a decision of the New York and Boston collectors that chemical glassware and chemicals do not come under the category of " scientific apparatus and preparations." This, however, is a freak of the Treasury Department and could be set right at Washington. As I wrote you, the " Ways and Means Committee" of 1870, in adopting that language, intended after full consideration to include all such materials under these terms and contemplated having them further defined by the Treasury Department. They were so defined at the motion of the chairman of the committee in a formal discussion which can only be set aside, according to their usage, on the recommendation of the Attorney-General. Now I am very sure it has never been set aside and all that is necessary in the premises to set things right is for some influential, person to see the Assistant Secretary and have the matter looked up. As I wrote I am one of a few, if not the only person who knows what the intentions of the committee of 1870 were, and if I can be of service in the matter with my testimony I shall be glad to do what I can.

<div align="right">Very truly,</div>

(Signed)   JOSIAH P. COOKE.

The law governing the decisions of the secretary referred to by Professor Cooke is probably the one found in S. L., Vol. 18, Chapter cxxxvi, of March 3, 1875, Section 2. " That no ruling or decision once made by the Secretary of the Treasury, giving construction to any law imposing customs duties, shall be reversed or modified adversely to the United States, by the same or a succeeding secretary, except in concurrence with an opinion of the Attorney-General recommending the same, or a judicial

decision of a circuit or district court of the United States conflict-
ing with such ruling or decision, and from which the Attorney-
General shall certify that no appeal or writ of error will be taken
by the United States : Provided, that the Secretary of the Treas-
ury may in his discretion, decline to aquiesce in the judgment,
decision, or ruling of an inferior court upon any question affecting
the interests of the United States, when, in his opinion, such
interests require a final adjudication of such question by the court
of last resort.''

The method of procedure for appraisement and contest as set
forth in Sections 10 *et seq.* of the Tariff Act of June 10, 1890,
shows that it is beyond the power of those poor institutions, that
most need the benefit of duty-free goods, to contest a decision of
an appraiser.

Effort has constantly been made by the customs officials to read
into the phraseology of the Tariff acts something else than its
plain and evident meaning. Naturally this has led to contests
and because of these the Secretary of the Treasury addressed the
National Academy of Sciences September 13, 1884, stating that
the appraiser had experienced great difficulty ''in determining
what instruments and other articles are entitled to classification
for duty as ' philosophical apparatus and instruments' under the
Tariff Act of March 3, 1883,'' and asking the Academy to report
''a list comprising the different articles which properly come
within the scope of the said statutory provision.''

The Academy reported (quoting the clause taxing philosophi-
cal apparatus and instruments, 35 per cent. *ad valorem*, and the
clause admitting philosophical and scientific apparatus, instru-
ments and preparations duty-free when imported for the use of
educational and other institutions) that '' the obvious intent of
Congress in specially designating philosophical instruments was
to cover the case of institutions and individuals who might import
the instruments and apparatus for the purpose of improving nat-
ural knowledge,'' and that it had not found it possible to prepare
the desired list in a way which would be at all satisfactory
because '' Firstly, an instrument is philosophical, not in conse-
quence of its special construction or function, but in consequence
of the uses to which it is to be put, and many instruments may be
put both to uses which are philosophical and to uses which are

purely industrial or commercial. Secondly, the number of differ-
ent kinds of philosophical apparatus is so great, and new kinds
are so constantly added, that an exhaustive enumeration is
impossible."—*Report Natural Academy of Sciences, 1884, pages
65-67.*

The following decisions of the Treasury Department as issued
for guidance of its appraisers show its attitude :

(9610)

Free entry—Surgical Instruments for Hospital.

TREASURY DEPARTMENT, September 5, 1890.

SIR : The Department is in receipt of your letter of the 28th
ultimo, reporting on the application of Mr. T. G. Wall, Superin-
tendent of the Presbyterian Hospital, for the free entry of certain
surgical instruments and apparatus imported for the use of said
hospital.

It appears from your report that the free entry of the articles
was refused by you on the ground that there was no school of
medicine attached to the hospital, and you cite the Department's
decision of January 17, 1881, in a similar case where no duty was
levied on instruments imported by the New York Hospital.

In said case it appears that a regular school of medicine was
attached to the hospital, and that fact was mentioned as a reason
for admitting the instruments to free entry.

The provisions of the free list, T. I., 759, exempts from duty
" Philosophical and scientific apparatus, instruments, and prepa-
rations......specially imported in good faith, for the use of any
society or institution incorporated or established for religious,
philosophical, educational, scientific, or literary purposes."

In view of the statement of Mr. Frederick Sturgis, trustee of
the hospital, that it is maintained for the two distinct purposes
of education and care of the sick poor, and that while it has no
school in the strict sense of that term, its amphitheater is a con-
stant resort of students who receive instructions from the senior
operating surgeons, and that thirteen class heads are constantly
accompanied by juniors who receive instructions from them, the
Department is of the opinion that the institution is entitled to the
benefits conferred by T. I., 759.

You are therefore authorized to admit the instruments and

apparatus in question to entry free of duty under said provision of law.

Respectfully yours,

GEORGE S. BATCHELLER.

Acting Secretary.

COLLECTOR OF CUSTOMS, NEW YORK, N. Y.

(10603)

Philosophical and Scientific Apparatus.

TREASURY DEPARTMENT, January 16, 1891.

SIR : I transmit herewith a copy of a decision of the United States Supreme Court, No. 86, of William H. Robertson, collector, etc., against Oswald Oelschlaeger, and No. 255, of Oswald Oelschlaeger against William H. Robertson which is partly in favor of the government and partly in favor of the importer.

The question involved was as to the classification, under the Tariff Act of March 3, 1883, of various instruments, used in the arts, or in laboratories, or for observation and experiment, etc., manufactured partly of metal, which were imported into your port in 1884, the defendant (collector) having subjected such articles to a duty of 45 per cent. *ad valorem*, under the provisions in Schedule C., Paragraph 216, of said Act, "Manufactures, articles, or wares not specially enumerated or provided for in this Act, composed wholly or in part of iron, steel, copper, lead, nickel, pewter, tin, zinc, gold, silver, platinum, or any other metal and whether partly or wholly manufactured," while the plaintiff, (importer) claimed that the articles were " Philosophical apparatus and instruments," and dutiable at the rate of 35 per cent. *ad valorem*, under Paragraph 475, Schedule M, of said Act.

It will be seen that by this decision, the rule laid down by the United States Circuit Court upon the trial of the cases in that Court is affirmed, and that thereunder the following specific articles (designated by the number of the exhibit as given in the decision) are decided to be dutiable at the rate of 45 per cent. *ad valorem*, as classified by the defendant (collector), *viz :*

No. 2. So-called trial box being a small microscope arranged in a brass frame with a slot, used commonly for the examination of textile fabrics, etc.

No. 3. Jewelers' magnifying glasses, adapted to fit the eye.

No. 7. Opera glasses.

No. 9. Magnifying glasses or low power microscopes with handle.

No. 10. Plano convex lens, unmounted, used in the construction of telescopes, opera glasses, etc.

No. 12. Ophthalmoscopes, instruments used by oculists for examining the interior of the eye, etc.

No. 13. Graphoscopes, being combination magnifying glasses and stereoscopes.

No. 14. Oculists' outfits, consisting of boxes containing a number of glass lenses, ground to different angles, etc.

No. 17. Dentists' specula,—small mirrors, mounted, with handles, for examining inside the mouth.

No. 19. Pocket batteries for physicians, a combination of electric battery and Ruhmkorff coil used by physicians.

No. 23. A small pocket compass.

No. 27. Thermometers mounted on glass.

No. 28. Ordinary thermometers, mounted on wood.

No. 29. Thermometers, minimum, for testing alcohol.

No. 31. Small thermometers (bric-a-brac), mounted on small pieces of metal, and arranged to put on plaques and fancy ornaments.

No. 32. Dairy thermometers, and hydrometers combined, used for measuring the density of fluids, at certain temperatures.

Nos. 34 and 35. Clinical thermometers, used by physicians, in their ordinary practice.

No. 36. Pocket thermometers with cover.

No. 41. Alcoholometers, used for measuring the specific gravity of alcohol.

No. 42. Urinometers, used by physicians in their practice.

No. 44. Spectacle lenses.

As to the following specified articles, however, the Court decided that they were philosophical apparatus or instruments and were dutiable at the rate of 35 per cent. *ad valorem*, as claimed by the plaintiff :

Nos. 1 and 1 1/2. Large compound microscopes with accompanying prepared slides, the microscopes being used for examining minute objects invisible to the naked eye.

No. 4. Astronomical telescopes on tripods.

No. 5. Single-barreled telescopes or marine glasses for examining objects at a distance.

No. 6. Double-barrel or marine glasses, used to examine objects at a distance.

No. 8. Small telescopes on brass tripods.

No. 11. Reflecting mirrors used in old telescopes.

No. 15 and 16. Stereopticons or magic lanterns, with accompanying slides.

No. 18. Grenet batteries, electric batteries for generating electricity, used largely in experiment.

No. 20. Inductive Ruhmkorff coils, used for a variety of purposes.

No. 21. Galvanometers, used for detecting electrical currents.

No. 22. Geissler tubes, used by scientists.

No. 24. Anemometers used for measuring velocity of the wind.

Nos. 25 and 26. Hygrometers, used for measuring moisture in the atmosphere.

No. 30. Maximum and minimum thermometers for recording temperatures.

No. 33. Laboratory thermometers, unmounted, used for scientific purposes.

Nos. 37, 38, 39. Aneroid barometers, used for measuring pressure and weight of the atmosphere.

No. 40. Hydrometers, used for obtaining specific gravity of liquids.

No. 43. Radiometers, used for illustrating the radiation of heat and light.

It will be noticed, that in reaching these conclusions the Court says that while " there is undoubtedly a clear distinction between mechanical implements and philosophical instruments or apparatus, ... it is somewhat difficult in practice to draw the line of distinction between the two classes, inasmuch as many instruments originally used only for the purpose of observation and experiment have since come to be used partially or wholly, as implements in the arts; and on the other hand, many implements merely mechanical are constantly used as aids in carrying on observations and experiments of a philosophical character," and that " in short, philosophical apparatus and instruments are such as are more commonly used for the purpose of making observations and discoveries in nature, and experiments for developing and exhibiting natural forces, and the conditions under which

they can be called into activity ; while implements for mechani-
cal or professional use in the arts are such as are more usually
employed in the trades and professions for performing the opera-
tions incidental thereto.''

It is also set forth in the opinion of the Court that the judge
in the Court below committed no error as to the character and
classification of the instruments respecting which he directed the
jury what verdict to render.

Upon due entry of the judgment in the Court below, in pur-
suance of the mandate of the United States Supreme Court, ·you
are hereby authorized to take the necessary steps for its settle-
ment, by forwarding the usual certified statement for the con-
sideration of the Department.

This decision will also apply to any other suits which may now
be pending at your Court, involving the same question, and the
course above indicated may be pursued as to them, provided, of
course, that the requirements of the statutes in force at the time
of their institution were fully complied with as to protest, appeal,
etc.

In reliquidating entries covered by said suits, however, care
will be taken to see that the distinction drawn by the Court
between the two classes of instruments is strictly observed, and
that only such articles as thereby come within the scope of the
provision in said Act of 1883 (Paragraph 475), for '' philosophical
apparatus and instruments,'' are reclassified at a duty of 35 per
cent. *ad valorem.*

<div align="right">

Respectfully yours,

WILLIAM WINDOM,

Secretary.
</div>

COLLECTOR OF CUSTOMS, NEW YORK, N. Y.

<div align="center">

(10607)

Boxes Containing Philosophical Apparatus.
</div>

<div align="right">

TREASURY DEPARTMENT, January 17, 1891.
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SIR : The Department received your letter of November 7th
last, submitting the appeal, 9311 *t*, of Messrs. J. W. Queen and
Co., from your assessment of duty at the rate of 45 per cent. *ad
valorem*, on certain so-called cartons containing philosophical
apparatus, imported by them per Indiana, February 11, 1890 (pro-
test filed prior to August 1, 1900), and claimed to be entitled to

exemption from duty under the provisions of Section 7, Act of March 3, 1883.

From the report of the appraiser it appears that the articles in question are not cartons or coverings, in the ordinary sense of the term, but that they form part and parcel of certain electrical instruments, being adapted to use only as parts of such instruments, the value being included in the invoice price, and that the instruments, including the boxes, were classified as entireties, as manufactures in part of metal, dutiable at the rate of 45 per cent. *ad valorem*, under the provisions of T. I., 216.

The claim that such cartons or boxes are entitled to free entry as coverings is therefore rejected and your assessment of duty thereon as parts of the instruments is hereby affirmed.

<div style="text-align:right">Respectfully yours,
O. L. SPAULDING,
Assistant Secretary.</div>

COLLECTOR OF CUSTOMS, PHILADELPHIA, PA.

<div style="text-align:center">(10619)</div>

Magic-Lantern Slides for Sunday School Purposes.

<div style="text-align:center">TREASURY DEPARTMENT, January 21, 1891.</div>

SIR : The Department is in receipt of a letter addressed to you by F. B. Swayne, of Toledo, Ohio, under date of the 14th inst., in which he inquires whether magic-lantern slides for Sunday School purposes, and to be the property of the church would be admitted free of duty under the statute providing for the admission without duty of philosophical apparatus, etc., which is to become the property of an educational or religious institution.

In reply, I have to inform you that the Supreme Court has recently decided that stereopticons, with accompanying slides, are philosophical apparatus and instruments, and as Paragraph 677, of the Act of October 1, 1890, exempts from duty " philosophical and scientific apparatus ...... specially imported in good faith, for the use of any society or institution incorporated or established for religious ...... purposes, ... and not intended for sale," the Department is of the opinion that such slides are entitled to exemption from duty if specially imported for the use of said society.

<div style="text-align:center">Respectfully yours,
WILLIAM WINDOM,
Secretary.</div>

Hon. William E. Haynes,
U. S. House of Representatives.

(10683—G. A. 267)

Free Entry—Articles for College—India-Rubber Tubing.

Before the U. S. General Appraisers, at New York, January 23, 1891.

In the matter of the protest, 1849 *a*, of Richard King and Co., against the assessment of duty by the collector of the port of New York, on '' India-rubber tubing,'' imported per Servia, August 13, 1890. —*Opinion by Sharretts, General Appraiser.*

The appraiser reports the merchandise to be the ordinary India-rubber tubing of commerce, suitable for various uses. Duty was assessed upon the same at 25 per cent. *ad valorem*, under T. I., 454. The appellants contend that the article was imported for the use of Cornell University, and is entitled to free entry as philosophical or scientific apparatus or instruments.

The importers were invited to appear before us and give evidence in substantiation of their claim, but having failed to do so, we assume the return made by the appraiser is correct ; and as India-rubber tubing, such as is designed for general use, is not philosophical or scientific apparatus or instruments within the meaning of the law, the fact that the importation in question is intended for use of a college, in connection with the class of apparatus or instruments provided for in T. I., 759, does not, in our opinion, affect the result. The action of the collector is accordingly affirmed.

(11045—G. A. 488)

Philosophical Instruments and Apparatus—Celluloid Labels for Plants not Free As.

Before the U. S. General Appraisers at New York, April 14, 1891.

In the matter of the protest, 3147 *b*, of Missouri Botanical Garden, against the decision of the surveyor of customs, at St. Louis, Mo., as to the rate and amount of duties chargeable on certain celluloid labels for plants, imported per Rugia, December 12, 1890.—*Opinion by Wilkinson, General Appraiser.*

The articles in question are celluloid tags or labels, imported by the Missouri Botanical Gardens, to be used in designating the names of various plants. The merchandise was assessed for duty

at 60 cents a pound and 25 per cent. *ad valorem*, under the provisio·· of Paragraph 21, Act of October, 1890, for finished articles made of collodion.

Appellants claim that the goods should be free of duty, under the provisions of Paragraph 677, as "·the said labels are ·the property of, and were consigned to and for the use of the Missouri Botanical Gardens, an institution authorized by an Act of the Legislature of the State of Missouri for scientific and educational purposes."

Paragraph 677 provides for philosophical and scientific apparatus, instruments, and preparations, and statuary, casts, paintings, drawings, and etchings, thus embracing but few of the many things used by an educational institution. This list does not include celluloid tags and, like hoes, watering pots, and many other implements used in a botanical garden, there is no provision of law to exempt them from duty.

The decision of the collector is therefore affirmed.

(11050—G. A. 493)

Philosophical and Scientific Apparatus—Cotton Cloth not Free As.

Before the U. S. General Appraisers at New York, April 15, 1891.

In the matter of the protest, 6223 *a*, of the Roosevelt Hospital, Jas. R. Lathrop, superintendent, against the decision of the collector of customs at New York as to the rate and amount of duties chargeable on certain so-called cambric flannel, imported per Slavonia, December 26, 1890.—*Opinion by Lunt, General Appraiser.*

The merchandise is invoiced as " 2 bale cambric, containing 50 pieces, 40 meters each, 48 inches wide." The appraiser returned the same as bleached cotton cloth not less than 50, and not exceeding 100 threads to the square inch, valued at over 9 cents per square yard, which return we find to be correct. Duty was levied thereon by the collector at 35 per cent. *ad valorem*, under Paragraph 345, N. T.

We also find that the importation is made by the Roosevelt Hospital, a charitable institution incorporated under the laws of New York for the relief of the sick, etc., treating them gratuitously if they are unable to pay. We also find that, since the

establishment of the hospital, medical students have been permitted to witness surgical operations there performed upon the patients, and that regular clinics are now held for students from the medical school of Columbia College. No distinct provision is made in the Act of Incorporation of this hospital for the medical instruction of such students.

It is claimed that the facts bring this hospital within the scope of the provisions of Paragraph 677, N. T., as a " society or institution incorporated or established for religious, philosophical, educational, scientific, or literary purposes," and that under said paragraph "philosophical and scientific apparatus, instruments, and preparations ...... specially imported in good faith, for its use and not intended for sale, may be admitted free of duty; that this cotton cloth is a preparation which such an institution is entitled to import free ; that it is to be torn into strips and used in the hospital for bandages."

Without undertaking to determine whether the Roosevelt Hospital is a society or institution incorporated or established for the purposes mentioned in Paragraph 677, a fair interpretation of the words " Philosophical and scientific apparatus, instruments and preparations," as contained in said paragraph, would exclude bleached cotton cloth from the category of philosophical and scientific preparations specified therein. The fact that the cloth is intended to be torn into strips and used for bandages does not change its character or commercial designation. It is simply cotton cloth suitable for many every-day uses, and not a philosophical or scientific preparation. We hold that the same was correctly classed as subject to duty at 35 per cent. *ad valorem*.

The protest is overruled and the action of the collector affirmed.

(14261)

Absolute Alcohol Imported for Colleges.

TREASURY DEPARTMENT, August 2, 1893.

SIR : The Department is in receipt of a letter, dated the 19th ultimo, from the United States attorney for the southern district of New York, in which he reports the trial, on the 18th ultimo, in the United States Circuit Court in his district, of a suit arising on the application of the collector of customs at New York, for a review of the decision of the Board of General Appraisers, as to

the rate and amount of duty on certain absolute alcohol imported
by Messrs. Richard King, and Co., per Russia, August 3, 1891,
suit No. 867.

It appears that the alcohol in question was classified by the col-
lector as alcohol testing 198 degrees, at the rate of $2.50 per
proof gallon, under the provisions of Paragraphs 329 and 333 of
the Act of October 1, 1890, the importers claiming that the same
was free of duty, under the provisions of Paragraph 677 of said
Act which is as follows :

" Philosophical and scientific apparatus, instruments, and prepa-
rations .... specially imported in good faith, for the use of any
society or institution incorporated or established for religious,
philosophical, educational, scientific, or literary purposes, or for
encouragement of the fine arts, and not intended for sale."

The importers claim that the article was absolute alcohol, and
as such was a scientific preparation within the meaning of the
above provision of law, and furthermore, that alcohol of this test
is a scientific preparation not manufactured for any other pur-
pose than scientific research work. The case went to the Board
of General Appraisers, where the decision of the collector was
reversed, whereupon the government appealed the case to the
Court, where the decision of the Board was affirmed, no opinion
being delivered.

The District Attorney, in reporting upon the case, states that
the testimony produced was to the effect that this absolute alco-
hol was used largely in laboratories and that the importers never
sold it to manufacturers or wholesale druggists, and never to col-
leges except for scientific preparations and that it was also proved
that the oaths of the officers of the institutions for which this
alcohol was imported were made in accordance with the instruc-
tions of this department of June 8, 1889 (synopsis 9424), the alco-
hol having been ordered specially for these institutions before its
importation.

The District Attorney further states that inasmuch as the
importers complied with all the requirements of the Department
in relation to the proof for which these importations were made,
the amount of commission charged by the importer, which was an
element of the prosecution in this case, did not in reality constitute
a sale of the merchandise in controvention of said Paragraph 677.

Upon submitting the matter to the Attorney-General, under the provisions of Section 15, of the Act of June 10, 1890, that officer advises this Department, under date of the 26th ultimo, that for the reason stated by the District Attorney no appeal will be directed by his Department from the judgment of the Circuit Court.

In view of the above you are hereby authorized to take measures looking to the payment of this judgment, and you will apply these instructions to all similar cases pending at your port where the parties have duly protected their rights in the manner provided by law.

Department's instructions of November 10, 1890 (synopsis 10359) are modified accordingly. In applying this decision it will be understood that all alcohol imported for scientific use is not necessarily free of duty, but only such as is of the character and test as that in question and none as "absolute alcohol," regarding which oaths are filed in accordance with the Department's circular above referred to.

Respectfully yours,

W. E. CURTIS,

(5718 f.) *Acting Secretary.*

COLLECTOR OF CUSTOMS, NEW YORK.

· (14381—G. A. 2265)

Absolute Alcohol—Free as a Scientific Preparation.

Before the U. S. General Appraisers at New York, August 23, 1893.

In the matter of the protest, 19706 *b*-8546, of E. H. Bailey and Co., against the decision of the collector of customs at Philadelphia, as to the rate and amount of duties chargeable on certain absolute alcohol, imported per Procida, March 8, 1893.—*Opinion by Somerville, General Appraiser.*

We find the merchandise to be "absolute alcohol," substantially identical in kind with the preparation covered by our decision G. A. 1368, in re. Richard Kny and Co., *et al.*

The article was assessed for duty under Paragraph 329 of the new Tariff Act as distilled spirits and is claimed to be free of duty under Paragraph 677, as a "scientific preparation" imported in

good faith, for the use of a college established for educational, scientific, or literary purposes.

We find that the merchandise was imported not for sale, but in good faith for the use of the University of Pennsylvania, which is an institution established for educational and scientific purposes, and further, that it is a scientific preparation within the meaning of said Paragraph 677, as defined in said Board decision G. A. 1368, which was affirmed on appeal by the United States Circuit Court for the southern district of New York (without opinion), on June 18, 1893, per Lacombe, J, and has since been fully acquiesced in by the Treasury Department.

The protest is sustained, the collector's decision reversed, and he is instructed to reliquidate the entry accordingly.

(21361)

Philosophical Instruments.

Arithmometers not philosophical instruments within the meaning of Paragraph 638, Act of July 24, 1897, and the decision of the United States Supreme Court in Robertson *vs.* Oelschlaeger (S. 10603), whether imported for industrial, mechanical, or educational purposes.

TREASURY DEPARTMENT, July 7, 1899.

SIR : Referring to your letter of the 22nd ultimo, reporting in regard to the classification of arithmometers imported at your port, I transmit herewith a copy of a letter addressed to the Felt and Tarrant Manufacturing Co., of Chicago, in which it is held that such articles are subject to duty at the rate of 45 per cent. *ad valorem*, under the provisions of Paragraph 193, of the Act of July 4, 1897.

It appears from the report of the appraiser at your port that such articles are returned as dutiable at 45 per cent. *ad valorem*, except when entered for colleges or educational purposes, in which case they have been admitted to free entry as philosophical instruments under the provisions of Paragraph 638, of the Act of July 24, 1897.

In the decision of the United States Supreme Court, in the case of Robertson *vs.* Oelschlaeger, January 16, 1891 (S. 10603), it is held that " philosophical apparatus and instruments are such as are more commonly used for the purpose of making observations

and discoveries in nature, and experiments for developing and exhibiting natural forces, and the conditions under which they can be called into activity, whilst instruments for mechanical or professional use in the arts are such as are more usually employed in the trades and professions for performing the operations incidental thereto.''

No distinction can be made in the classification of such articles when imported for industrial uses, or for educational purposes, as the same are instruments of an industrial or mechanical nature, and not philosophical instruments within the above definition. You will be governed accordingly.

Respectfully yours,

O. L. SPAULDING,

(4630 i.) *Assistant Secretary.*

COLLECTOR OF CUSTOMS, NEW YORK, N. Y.

(21770)

Philosophical Instruments and Preparations.

Under the provisions of Paragraph 638, Act of 1897, and the decision of the United States Supreme Court in the Oelschlaeger case (T. D. 10603) only such instruments can be admitted to free entry as philosophical instruments '' as are used for the purpose of making observations and discoveries in nature and developing and exhibiting natural forces and the conditions into which they can be called into activity,'' and the '' preparations,'' referred to in said paragraph must be scientific or philosophical in their nature, and can only be admitted to free entry when used wholly in conducting philosophical or scientific researches. Surgical instruments and medicinal preparations are excluded from free entry under the above ruling.

TREASURY DEPARTMENT, November 16, 1899.

SIR : The Department is in receipt of your letter of the 11th instant, in regard to your action in admitting to entry, free of duty, under the provisions of Paragraph 638, of the Act of July 24, 1897, a certain gas or ether inhaler, imported for the Chicago Clinical School of Medicine. You refer to a letter of this Department of the 5th instant, addressed to the auditor of the Treasury Department, a copy of which has been furnished you, in which it is stated, that under the decision of the United States Supreme

Court, in the case of Robertson, Collector, *vs*. Oelschlager (T. D. 10603), and the Department's ruling of July 7, 1899 (T. D. 21361), the instrument in question is not classifiable as a philosophical instrument and that the entry should be reliquidated and a call made upon the importers for duties on the article in question.

Paragraph 638 of the Act of 1897 provides as follows :

Philosophical and scientific apparatus, utensils, instruments, and preparations, including bottles and boxes containing the same, specially imported in good faith, for the use and by order of any society or institution incorporated or established solely for religious, philosophical, educational, scientific, or literary purposes, or for the encouragement of the fine arts, or for the use or by order of any college, academy, school, or seminary of learning in the United States, or any state or public library, and not for sale, subject to such regulations as the Secretary of the Treasury shall prescribe.

And it is held that the words " philosophical and scientific " qualifies the succeeding words, "utensils, instruments, and preparations " (T. D. 11050.).

The Supreme Court in the above decision uses the following language :

Philosophical apparatus and instruments are such as are more commonly used for the purpose of making observations and discoveries in nature, and experiments for developing and exhibiting natural forces, and the conditions under which they can be called into activity, whilst implements for mechanical or professional use in the arts are such as are more usually employed in the trades and professions for performing the operations incidental thereto.

Without receding from the position taken by the Department in the matter, that the inhaler in question is not a philosophical instrument, I have to state that in view of the fact that there is some ground for such classification, as the instrument is a new invention, in a measure intended for experimental purposes in the treatment of tubercular cases, and differs materially from the ordinary gas and ether inhalers used generally by physicians, surgeons, and dentists, for the purpose of administering gas and ether to patients, thus showing a use " in making observations and discoveries in nature," and in view of the Department's

rulings of April 12, 1879 (T. D. 3972), and May 27, 1896 (T. D. 17142) no proceedings need be taken in this case looking to a collection of the duties on this instrument in question ; but duties should be assessed on future importations of this kind, leaving the importers to their remedy by protest under the provisions of Section 14, of the Act of June 10, 1890, when the question can be definitely settled by the Board of General Appraisers and the Courts. The reference in your memorandum to the Department's decision of September 5, 1889 (T. D. 9610) wherein it is held that certain surgical instruments and apparatus are free of duty as philosophical instruments, is not applicable to this case, as the decision of the United States Supreme Court, which defines the term "philosophical and scientific apparatus" was rendered subsequently thereto.

It is observed that you have also admitted to free entry as philosophical instruments, preparations, etc., such articles as anti-toxine, a low priced microscope, a gas arm, chemical scales "influenze" machine, and chemical thermometers, chloroform, alum, cobalt, lithium, magnesium, zinc, sulphur, caustic potash, acid acetate (sic.), ether, alcohol, carbonic acid, etc. Under the above definition none of these articles would appear to be entitled to free entry as philosophical or scientific apparatus, instruments, or preparations, unless the alcohol is found to consist of absolute alcohol (T. D. 14261 and 14381) and the microscope is found to belong to the class of "large compound microscope .... used for examining minute objects invisible to the naked eye" (T. D. 10603). The fact that the chemical preparations mentioned may be used for philosophical and scientific investigations will not operate to allow their admission under the provisions of Paragraph 638, unless they are actually imported for use in conducting scientific investigations, and not for use as medicinal or surgical preparations in the treatment of hospital patients.

You will be governed accordingly and assess duty on future importations of this nature made at your port.

Respectfully,

O. L. SPAULDING,

(6882 i.) *Assistant Secretary.*

COLLECTOR OF CUSTOMS, CHICAGO, ILL.

In Treasury Decisions, Vol. 3, No 25, of June 21, 1900, there

is published a compilation of paragraphs of the Act of July 24, 1897, articles of the customs regulations and rulings of the Treasury Department and the courts relating to the free importation of articles for institutions. It should be noted that rulings and decisions against merchants are made to apply to institutions.

Officers of institutions who have had difficulties in securing the benefit of the act are requested to communicate with Professor J. H. Long, 2421 Dearborn St., Chicago, Illinois.

Respectfully submitted,

CHARLES E. MUNROE,

Chairman.

SECOND ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

To the American Chemical Society :

Your committee upon international action with reference to standard atomic weights, has the honor to submit the following report. Since our report of a year ago,[1] various other societies have taken part in the discussion ; and in the coordination of their work, the German Chemical Society has rendered important service. Partly through the initiative of the latter organization, and partly through the agency of our own Society, a large international committee has been formed, and some of its deliberations are already before the chemical world for consideration.

On March 30, 1899, the special committee of the German Chemical Society, Professors Landolt, Ostwald, and Seubert, issued an invitation to other organizations having an interest in chemistry to appoint delegates to the international body. At the December meeting of 1898, the American Chemical Society had already taken action, and your present committee was appointed. The American Academy of Arts and Sciences also designated representatives, and important societies in Germany, Austria Hungary, Belgium, England, Switzerland, Italy, Japan, Holland, Russia, and Sweden also accepted the invitation. A body of 57 representative chemists was thus formed ; but France, Norway and Denmark do not appear in the list. We are informed, however, that the Chemical Society of Paris has recently appointed dele-

[1] This Journal, 22, 70.

gates, and their names will doubtless appear in the next report
of the International Committee. Another committee of three
was also named by the Fourth International Congress of Applied
Chemistry, which met in Paris during the last week of July, 1900.

In October, 1899, the committee of the German Chemical
Society sent to each of the international delegates a circular letter
proposing three questions. These questions were as follows :

1. Shall $O = 16$ be fixed as the future standard for the calcula-
tion of atomic weights?

2. Shall the atomic weights be given with so many decimals
that the last figure is certain within half a' unit, or what other
procedure shall be adopted ?

3. Is it desirable that a smaller committee should be formed,
which should undertake the continual revision of the yearly
atomic weight table and its publication? In case of agreement
upon this point it is proposed that each association shall name a
single delegate to the smaller committee.

To these questions forty-nine replies were received. As regards
the first question, forty chemists favored the oxygen standard,
seven preferred to retain the hydrogen unit, and two were willing
to accept either or both standards. The replies are published in
full,[1] some writers giving only categorical answers, and others
citing arguments in behalf of the position which they favored.
The majority for the oxygen standard was overwhelming ; but,
as we shall see later, it has not yet been universally accepted as a
final decision. At the Congress of Applied Chemistry, in the
section devoted to analytical chemistry, the question was dis-
cussed, and in this case the decision of the International Com-
mittee was sustained. As only two members of the latter com-
mittee were present at this discussion, representing opposite
sides, the action of the congress is to be regarded as a ratification
of the decision, and not as a mere duplication of votes by the
same men. An attempt was made to secure an actual meeting of
the International Committee at the congress, but it did not suc-
ceed. Too few of its members were in attendance.

The second and third questions of the German Committee were
also answered affirmatively, by a large majority in one case, and
unanimously in the other. Balloting for the smaller committee

[1] *Ber. d. chem. Ges.*, **33**, 1853 (1900).

has already taken place, and the result will probably be known before this report is presented. As to the second question, the replies and printed criticisms seem to indicate some misunderstanding as to its real significance ; and for this reason it ought to receive further and more careful consideration. In the opinion of your committee atomic weights should be printed with so many decimals as have any real significance, even though, in the calculation of ordinary analyses, rounded-off values may be employed.

In spite of the great majority given in the International Committee in favor of O = 16 as the standard for atomic weights, a vigorous protest against the decision has been made. In the original balloting, the seven dissentients were one American and six German chemists, the latter being delegates from the Verein Deutscher Chemiker. These six chemists, Bredt, Erdmann, F. Fischer, Volhard, Winkler, and Wislicenus, issued a new circular letter,[1] addressed to the teachers of chemistry in the German universities and technical schools, asking for a further and fuller expression of opinion. At the date of writing, the result of this canvass has not been published ; but Professor Erdmann, in a letter dated November 23, 1900, informs us that 143 replies have been received, of which 118 favor the retention of the older standard, H = 1. In the new edition of Erdmann's "Lehrbuch der anorganischen Chemie," this standard is adopted throughout, and other voices have also been raised in protest against O = 16. A pamphlet by Lassar-Cohn[2] furnishes a case in point, and another paper by Dr. A. R. L. Dohme[3] is noticeable as foreshadowing the probable action of the committee for the decennial revision of the United States Pharmacopoeia. In this important work the hydrogen scale is likely to be adopted.

From what has been said so far, it is evident that chemical opinion is still divided on the question of the basis for atomic weights, and that the desired unity of action has not been reached. Neither standard can be forced into general acceptance and further discussion is unavoidable. Even your own committee is divided upon the subject, and therefore asks from the members

[1] See *Ztschr. angew. Chem.*, July 24, 1900 ; *Chem. News*, August 10, 1900.

[2] "Ueber der Ungeeignete der Newendings für die Berechnung der Atomgewichte vorgeschlagenen Grundzahl 16.000." Hamburg (Voss), 1900.

[3] *Druggist's Circular and Chemical Gazette*; September, 1900.

of the American Chemical Society, an expression of their prefer-
ences. In order to facilitate such an expression we submit the
following summary of arguments which have been used for and
against each standard. These may be classified as historical,
theoretical, and arguments from convenience,[1] even though the
three categories are not absolutely separable.

Historically, it is urged, the hydrogen unit has the advantage
of being the original Daltonian standard; and except temporarily,
during the Berzelian period, it has been almost universally recog-
nized. Berzelius made oxygen the standard, and based his scale
upon $O = 100$; but oxygen as 16, considered as a basis for
atomic weights, is a recent innovation. It is true that the atomic
weight of oxygen, referred to hydrogen as unity, was long
thought to be 16, but this belief is now known to be an error.
To the believer in precedent and priority the adoption of the oxy-
gen standard would seem to be the perpetuation of an error, as
well as a break in the historical continuity of science.

To the advocates of oxygen as a basis for atomic weights the
foregoing argument appears to be irrelevant and fallacious. They
claim that hydrogen has only been a nominal unit, since actual
determinations of atomic weight are commonly referred to hydro-
gen through the medium of oxygen, the latter being the experi-
mental standard of reference. To retain the hydrogen scale
means to take the ratio H : O as a fundamental base line ; and
every change in that implies changes throughout the entire table.
Historically, at least as viewed from the experimental side of the
question, hydrogen has been only the theoretical standard ; oxy-
gen, taken as 16, has been the real basis for calculation. The
ordinary, familiar atomic weights are all in harmony with the
oxygen basis, and, with other constants which rest upon the same
foundation, they permeate all chemical literature. The retention
of the hydrogen unit implies confusion in the interpretation of a
great mass of recorded data ; and apparent historical conserva-
tism really involves wide-spread and radical change. After all,
the historical argument tends to obscure the essential issue, the
true problem being the establishment, on a permanent basis, of
the best possible scale.

[1] For an elaborate argument in favor of the oxygen standard, see Richards: *Am. Chem.
J.*, **24**, 377 ; see also Brauner: *Ztschr. anorg. Chem.*, **26**, 186.

On theoretical grounds it is claimed that the hydrogen unit is the most natural basis for atomic weights, partly because the hydrogen atom is the lightest atom known, and partly because hydrogen is also the standard for gaseous densities and for valence. The atomic weight scale and the density scale rest upon the same foundations ; and if the oxygen standard is adopted, then all vapor-densities must be changed to a corresponding degree. Furthermore, unity, or some number logarithmically equivalent to unity, such as 10 or 100, would seem to be a better starting-point for calculations than some other quantity, arbitrarily chosen, whose selection might be troublesome to explain. An approximate unity, like 1.008, is meaningless, and the value 16.000, taken as a standard, can only be explained by reference back to hydrogen, the unit from which it was originally derived. The explanation, then, is somewhat in the nature of an apology, and concedes much to the opposite side.

To the theoretical arguments the advocates of the oxygen scale attach little importance, regarding the question as one of practice and convenience rather than as one of theory. They point out, however, that elements lighter than hydrogen may yet be discovered, and that then the theoretical considerations would be radically changed. If Prout's so-called law held good, a valid reason for the hydrogen unit would exist ; but as matters stand now that unit is as arbitrary as any other, and rests upon no necessary foundation of principle. Which standard, then, is the more convenient for general use?

The answers to this question suggest two quite distinct points of view ; that of the teacher on the one hand, that of the laboratory chemist on the other. The teacher argues in favor of the hydrogen unit, that it is easily intelligible to beginners, whereas the oxygen standard is somewhat difficult to explain. The difficulty, moreover, becomes greater when gaseous densities are considered, and the teacher is forced to decide whether he shall adopt a dual standard, or reject the hydrogen basis altogether. A few teachers claim that these difficulties are much overrated, while others propose to evade them, either by giving to the beginner round numbers which are confessedly approximate, or by abandoning hydrogen as a standard of specific gravity and taking oxygen instead. If the latter policy were followed it

might lead to discordance between the allied sciences of chemistry and physics, for the physicist prefers hydrogen as a standard because it is not only the lightest of all substances, but also the one which most nearly approaches the ideal perfect gas. In the hydrogen thermometer its nearly uniform rate of expansion is considered, as well as the fact that at low temperatures it is the last gas except helium, to assume the liquid state. The graduation of the hydrogen thermometer is the ultimate standard of reference in all exact thermometry, whether for low temperatures or for high. This question of harmony between different branches of science is one which needs to be seriously considered ; and so far, at least as regards our choice of atomic weights, it seems not to have been adequately discussed.

When we consider the use of atomic weights in the calculation of analyses, the oxygen table has the great advantage of familiarity to chemists, and perhaps also the minor advantage that a larger proportion of the values are nearly integers. The latter consideration, however, is of little importance, for many analysts use tables of logarithms or of factors ; but to the chemist who employs atomic weights directly, integral numbers are more easily remembered than figures which involve one or two decimal places. In commercial work the ordinary round numbers are likely to hold their own, and no serious inaccuracy of results is to be feared from this practice. The usual errors of analysis far outweigh any uncertainty of calculations which may be due to neglect of decimals in the commoner atomic weights. There are cases to which this argument does not apply, and in which a greater exactness of data is indispensable ;[1] but these are few in number and should be known to the specialist in whose practice they arise.

The unfamiliarity of the hydrogen scale is easily illustrated by the following table, in which a few of the more common atomic weights, as given under both standards, are compared :

[1] See " Fourth Annual Report of the Committee on Atomic Weights," This Journal, 19, 359, May, 1897, with reference to the commercial assay of chrome iron ore.

	H = 1.	O = 16.	Difference.
Hydrogen	1.000	1.008	0.008
Oxygen	15.879	16.000	0.121
Chlorine	35.18	35.45	0.270
Potassium	38.82	39.11	0.290
Copper	63.10	63.60	0.500
Bromine	79.34	79.95	0.610
Silver	107.11	107.92	0.810
Iodine	125.89	126.85	0.960
Barium	136.40	137.40	1.000
Mercury	198.50	200.00	1.500
Lead	205.36	206.92	1.560

The difference increases with increasing atomic weight, and amounts in each case to about 0.75 per cent. of the entire value. With small atomic weights the difference appears trifling; in the higher parts of the table the discordance is much more evident.

Clearly then, the adoption of the modern hydrogen scale would compel chemists to drop certain old values and to learn the new. Whether this is desirable or undesirable is for chemists to decide. To the older chemists, who first learned the Daltonian equivalents, and then discarded them for the atomic weights of Cannizzaro, the change will not seem difficult ; to the younger men the anticipation of annoyance is likely to be worse than the reality. At all events, the inconvenience, be it great or small, is evident, and it must be taken into account in arriving at the final conclusion.

Your committee hope that the members of the American Chemical Society will consider the questions and considerations which are presented in this report, and express their views upon them. Which system of atomic weights is the better, not merely for temporary purposes, but regarded broadly, with a view to the permanent interests of science? That is the real question upon which a consensus of opinion is desired, and which ought to be considered from all points of view. Replies should be addressed to the chairman of this committee, F. W. Clarke, U. S. Geological Survey, Washington, D. C., before June 1, 1901.

Respectfully submitted,

F. W. CLARKE,
J. W. MALLET,
EDWARD W. MORLEY,
THEO. W. RICHARDS,
EDGAR F. SMITH.

REPORT OF THE COMMITTEE ON PATENT LEGISLATION.

To the Council of the American Chemical Society :

GENTLEMEN : Your committee begs leave to report that the following bills are now before Congress :

S. 5026. "To revise the laws of the United States relating to trade-marks."

S. 5027. "To regulate and protect marks, trade-marks, commercial names, and symbols used in commerce, and to enforce treaties regarding the same."

S. 5028. "Respecting applicants for patents not residing in the United States."

S. 5029. "To give effect to treaty stipulations relating to letters patent for inventions."

S. 5030. "To revise the patent laws of the United States."

S. 5026 was prepared by Judge Greeley, and S. 5027 by Mr. Forbes and Judge Grosscup, all of the commission appointed by the President of the United States "to revise the laws relating to patents, trade-marks, and trade names, with reference to existing conventions and treaties." The relative merits of these bills are discussed in the *Scientific American*, December 15, 1900, p. 371. It is generally believed that the divergence of views between these bills is so great that no action will be taken upon them at this session. It is understood that the authorities of the patent office favor S. 5028 and S. 5029, but doubt the propriety of S. 5030, which extends the rights of foreign inventors.

Through the courtesy of Judge Greeley, your committee has been favored with a typewritten copy of the report of the commission, which will probably soon be printed by Congress, and certain literature, relative to phases of the law, which had been submitted to the commission. Chemists are recommended, especially to read that part of the report following the legend "Classes of Inventions Excluded from Protection," as the commission was urged to recommend "that the United States law should be amended *to exclude* from patent protection both medicines and *chemical products* generally, at least so far as such inventions are the inventions of subjects or citizens of the foreign countries which exclude these classes of invention from patent protection." Attention is also called to the "Argument of E. N.

Dickerson before the Commission,'' and to the pamphlet entitled
'' Trade-marks, Patents, and Pharmaceutical Reforms,'' published
for gratuitous distribution by the Philadelphia Medical Pub-
lishing Co., especially to that part of the latter treating of
''Product Patents *vs*. Process Patents.''

We add the following letter from our secretary, to whose influ-
ence and on whose initiative the appointment of this committee
was largely due.

BROOKLYN, N. Y., December 24, 1900.

Prof. C. E. Munroe, Columbian University, Washington, D. C.

DEAR SIR : I have been away for some time and have had to
neglect the Patent Committee. I have sent your letter to one of
our most efficient members and have been in communication with
some of the others. I could not get a meeting, but they all agree
so far in recommending rather a waiting policy, as regards intro-
ducing new matter, fearing that some injurious action might be
taken in Congress if the matter was once started.

They endorse, however, all of them, the recommendations of
Grosscup Committee, as they have been reported in the papers,
and also the International Association, which met at Brussels
lately, and recommend the members of the Chemical Society to
use their influence in promoting a passage of these recommenda-
tions. They also think that some standing committee should be
maintained to be on guard against injurious legislation if the
need should come up.

Yours truly,

C. C. PARSONS.

(Dictated.)

Respectfully submitted,

CHARLES E. MUNROE,

Chairman.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical
Society was held at the Chemists' Club, 108 W. 55th St., New
York City, November 16, 1900. The meeting was called to order
by President McMurtrie, at 7.20 P.M. There were present Messrs.
McMurtrie, Hale, Chandler, Doremus, Hallock, and Smith.

It was voted that the librarian be instructed to transmit to the
Royal Academy of Science, in Amsterdam, an acknowledgment
of the receipt of their proceedings, and also a full set of the Jour-
nal and Proceedings of the American Chemical Society, and to
continue an exchange of publications with them.

The librarian was authorized to purchase a desk for his use at a cost not to exceed $35.

An appropriation of $15 was made to defray the expenses of printing a circular letter to be used by the Committee on Advertising.

The Board then adjourned.

ALBERT C. HALE, *Secretary.*

COUNCIL.

The Council of the American Chemical Society met in the chemical lecture room of the Lewis Institute, Chicago, Ill., at 1.45 P.M., Thursday, December 27, 1900. There were present Messrs. McMurtrie, Hale, Hart, Prescott, Munroe, Long, McPherson, Sabin, W. A. Noyes, Freer, and Springer.

The minutes of previous meetings were adopted as recorded by the secretary. It was voted that the summer meeting be held in Denver, Colo., August 26 and 27, 1901, and that the secretary inform the secretary of the American Association for the Advancement of Science of this action.

Informal communications in reference to future meetings were announced by the secretary.

The secretary presented a communication from C. A. Doremus, chairman of the New York Section, stating that the executive committee of that section would recommend to the members of the Section at its next meeting that they invite the Society to hold its 25th anniversary in New York City. The Council directed the secretary to thank Dr. Doremus for the communication, and the matter was referred to the Committee on the Twenty-Fifth Anniversary.

It was voted that all nominees for membership up to the close of this meeting of the Society, be considered as acted upon by the Council, and the secretary was instructed to declare them elected whenever all the other requirements of the constitution in regard to them as nominees should have been met.

The following persons were nominated to fill the respective positions designated as officers and members of the standing committees of the Society for the year 1901 :

Secretary—Albert C. Hale.

Treasurer—A. P. Hallock.

Librarian—E. G. Love.

Editor—Edward Hart.

Councilor—(In place of F. W. Clarke, president-elect), W. B. Rising.

Directors—(To serve two years, beginning January 1, 1901), C. A. Doremus, C. B. Dudley.

Committee on Membership—Wm. McMurtrie, M. T. Bogert, C. L. Reese.

Finance Committee—Elwyn Waller, J. H. Wainwright, D. Woodman.

Committee on Papers and Publications—Edward Hart, W. F. Hillebrand, J. H. Long, Wm. McMurtrie, A. A. Noyes, W. A. Noyes, E. F. Smith, H. N. Stokes, H. P. Talbot, H. W. Wiley.

The report of the Committee on Estimates was presented by the secretary. Action upon it was postponed until the report of the Committee on Title Index should be presented. Wm. McMurtrie, chairman of the Committee on Title Index, presented a report for that committee. C. E. Munroe moved that the report of the Committee on Title Index be accepted, and that $1,000 be appropriated for the purpose of preparing abstracts of chemical literature. Mr. Freer moved as a substitute that the sum of $600 a year be appropriated for the preparation of reviews of chemical work in the various branches, the sum to be expended at the direction of the Committee on Papers and Publications. The vote on Dr. Freer's substitute was a tie, and the chairman casting his ballot against it, it was lost. Professor Munroe's motion was then carried, and on further motion by Professor Munroe the matter was placed in the hands of the Committee on Papers and Publications.

It was voted that an edition of 2700 copies of the Journal be printed for the months of January, February, and March, and 2500 for the balance of the year.

The following named sums in the budget were voted for the objects respectively designated :

$5,000 for Journal and reprints,

   225 for Directory,

   325 for general meetings,

   100 for the president's office,

  1,300 for the secretary's office,

400 for the treasurer's office,

310 for the editor's office,

50 for exchange list,

400 for completing and binding sets in the library,

200 for the librarian's office,

100 for clerical help for the librarian,

30 for the Membership Committee.[1]

It was voted that the secretary collect the membership dues as heretofore, and that he be allowed 10 per cent. commission on all dues collected as compensation for his work. It was voted that the secretary distribute at his discretion the amount appropriated for his office.

The Directors were authorized to appropriate for any special purpose or purposes, as may be necessary, amounts not to exceed in the aggregate $300. On motion of Dr. Munroe it was voted that the Board of Directors be recommended to appropriate $11,590 to be apportioned as set forth in the successive resolutions adopted by the Council at this session, it being understood that only so much of each sum shall be expended as shall be necessary to attain the desired object.

It was voted that F. W. Clarke and E. E. Ewell be delegated to see the speaker of the House of Representatives and others, with regard to the Standardizing Bureau Bill. It was voted that we recommend to the Directors that educational institutions be

[1] The various appropriations in the budget for 1901, may be expressed in tabular form as follows:

Journal and reprints	$ 5,000
Abstracts	1,000
Collection of dues (estimated)	900
Local sections (estimated)	1,250
General meetings	325
Directories	225
President's office	100
Secretary's "	1,300
Treasurer's "	400
Librarian's "	200
Clerical help for librarian	100
Completing and binding sets in library	400
Editor's office	310
Exchange list	50
Membership Committee	30
	$11,590
Special appropriations by Directors (if necessary)	300
Total	$11,890

allowed the same discount on sets of Journals as is given to dealers.

It was voted that a complete set of the Journal and proceedings be bound and sent to the editor to keep on file at his office.

It was voted that the secretary complete two sets of the lists of membership of the Society from the beginning, if possible, and that they be bound and kept in two distinct places. The Council voted to recommend to the Society that the question of taking any action on the metric system be laid upon the table.

The Committee on Standards for Instruments of Measure reported progress by Dr. Munroe. Dr. Munroe reported also for the Committee on Patents and Patent Legislation. The report was accepted and the committee continued.

Dr. Hart reported progress for the Committee on Exchanges.

Dr. Munroe, chairman, presented a voluminous report for the Committee on Duty-free Importation. It was voted that the report be published in full in the Proceedings of the Council, and that 200 reprints of it be made for the use of the Committee.

Dr. McMurtrie, chairman of the Committee on Twenty-Fifth Anniversary, reported progress. He also reported progress for the Committee on Advertising.

Consideration of the matter of a new contract for printing the Journal was postponed to an adjourned meeting which should be held immediately after the president's address.

The Council then adjourned to meet immediately after the delivery of the president's address.

ADJOURNED MEETING.

The president called the Council to order at 9 P.M., in the Banquet Hall of the Auditorium Hotel. Present, Messrs. McMurtrie, Hale, Sabin, Prescott, Springer, Munroe, W. A. Noyes, McPherson, and Long.

Dr. McMurtrie, chairman of the Committee on New Contract for Printing the Journal presented the results of the work of that Committee. He read bids and specifications on publishing the Journal from various firms and companies, and exhibited samples of paper submitted with the bids.

It was voted that the Committee on Contract is hereby authorized to close the contract for printing the Journal on behalf of the

Society, and that it is the opinion of the Society that the contract should be made with The Chemical Publishing Co., provided that the Company can subscribe to the specifications of the Committee, and that the paper shall be of a character and quality equal to that submitted by the New Era Publishing Company.

It was voted that the contract for printing the Journal be signed on behalf of the Society by the president, the secretary, and the treasurer.

It was voted that the Council recommend to the Board of Directors to make such arrangements as to rent for storage as may be equitable.

The Council then adjourned.

ALBERT C. HALE, *Secretary.*

NAMES PROPOSED FOR MEMBERSHIP.

Atkinson, James P., 36 Washington Square, West, New York City.

Axson, Edward W., Mannie, Tenn.

Bermingham, John, Jr., Pinole, Contra Costa Co., Cal.

Eldred, Frank R., Butte, Mont.

Gordin, Harry M., 502 E. 3rd St., Cincinnati, Ohio.

Rust, Robert R., Bound Brook, N. J.

Smith, Theodore E., 221 W. 83rd St., New York City.

Twieg, Wm. C., Pinole, Contra Costa Co., Cal.

CHANGES OF ADDRESS.

Barrows, W. A., Jr., Shenango Furnace Co., Sharpsville, Pa..

Bernhard, Adolph, Stone Creek, Ohio.

Bolling, Randolph, Crozer Furnaces, Roanoke, Va.

Brinker, H. L., 322 North Ave., Youngstown, Ohio.

Caldwell, T. O., Gilt Edge, Mont.

Calvert, J. E., Etna, Allegheny Co., Pa.

Campbell, Archibald, 3140 Durrell Ave., Walnut Hills, Cincinnati, O.

Coggeshall, G. W., 3 Chestnut St., Dedham, Mass.

Hamlin, Addison, North Blanchard, Me.

Hicks, Edwin F., 361 W. 27th St., New York City.

Hough, George J., care Mexican Copper Co., Ramos, San Luis Potosi, Mexico.

Maxwell, Dr. Walter, care Dept. of Agr., Brisbane, Queensland, Australia.

Norman, Geo. W., Gen. Chem. Co., Moro Phillips Works, Camden, N. J.

Norton, Hon. Thomas H., Consul des Etats-Unis, Mezreh, Mamouret-ul-Aziz, Turkey in Asia. Open mail *via* London and Constantinople.

Peckham, S. F., Room 104, 280 Broadway, New York City.

Perkins, T. S., care Cal. Tartar Wks., 123 California St., San Francisco, Cal.

Quinan, K. B., care De Beers Explosive Works, Cape Town, S. Africa.

Reese, H. J., Bozeman, Mont.

Smith, Burnett, 211 Franklin, Univ. of Pa. Dormitories, Philadelphia, Pa.

Stillwell, J. S., 156 Broadway, New York City.

Torrey, Chas. A., Jr., "Security Safe Deposit Vaults," Boston, Mass.

Williams, L. S., 6806 Wentworth Ave., Chicago, Ill.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The fifteenth meeting was called to order in the John Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., November 15, 1900. Thirty members and visitors were present.

Owing to the absence of the chairman and secretary, Dr. Henry Leffmann and Mr. W. T. Taggart were elected to fill the vacancies for the evening. Dr. Leffmann, in behalf of the Chemical Section of the Franklin Institute, extended an invitation to the Section to a meeting which will take place Thursday evening, November 22, 1900. It was moved and seconded that the invitation be accepted. Carried.

Dr. John Marshall was nominated to succeed himself as councilor.

It was moved and seconded that the secretary cast one ballot for the election of the nominee. The ballot was cast and Dr. John Marshall was declared elected councilor for the ensuing year.

The papers of the evening were : "The Atomic Weight of Antimony," by Dr. Edgar F. Smith ; "The Electrolytic Oxidation of Pyroracemic Acid," by G. W. Rockwell—read by Dr. Edgar F. Smith ; "Notes on the Composition of Some High Class Milks," by Dr. Henry Leffmann; "Exhibition of Specimens of High and Low Explosives, with Remarks Thereon," by Dr. Henry Leffmann.

Dr. Edgar F. Smith exhibited specimens of artificial silk made from the pulp of spruce wood, and also a substitute for celluloid, from the same source.

There being no further business the meeting adjourned at 9.30 P.M.   F. E. DODGE, *Secretary.*

MICHIGAN SECTION.

The Michigan Section met at the chemical laboratory of the University of Michigan, Friday, February 8, at 8 P.M. The paper of the evening was given by Professor Freer, on "Benzoylacetyl Hyperoxide." After a brief address by the retiring presiding officer, Professor Prescott, officers were elected for the following year. Professor Prescott declined a renomination and Professor Freer was unanimously elected to succeed him.

The list of officers is as follows : Presiding Officer, P. C. Freer, Ann Arbor ; Secretary-Treasurer, Alfred H. White, Ann Arbor ; Councilor, E. D. Campbell, Ann Arbor ; Executive Committee, the presiding officer and secretary, *ex-officio* ; John M. Francis, Parke, Davis & Co., Detroit ; A. F. Shattuck, The Solvay Process Co., Detroit ; David L. Davoll, Peninsular Sugar Co., Caro.

ALFRED H. WHITE, *Secretary.*

WASHINGTON SECTION.

The regular meeting was held on January 10, 1901. The following officers were elected for the ensuing year : President, V. K. Chesnut ; Vice-Presidents, W. F. Hillebrand and F. K. Cameron ; Secretary, L. S. Munson ; Treasurer, F. P. Dewey ; additional members of the Executive Committee, H. N. Stokes, H. C. Bolton, E. E. Ewell, and L. M. Tolman.

WILLIAM H. KRUG, *Secretary.*

Proceedings

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Hotel Endicott, 101 W. 81st Street, New York City, February 8, 1901. There were present Directors Clarke, Doremus, Dudley, Hale, Hallock, and Smith, and also Drs. Hart and McMurtrie. The meeting was called to order at 4.10 P. M.

The sum of $11,590, or so much thereof as may be necessary, was appropriated to defray the expenses of the Society for the year 1901, in accordance with the budget adopted by the Council at the meeting held in Chicago, December 27, 1900.

The librarian was directed to loan to the secretary such numbers of the Journal and Proceedings as the secretary might need in preparing a history of the Society.

The sum of $11.62 was appropriated to reimburse Albert C. Hale for cash paid for cablegram of congratulations to Dr. Vladimir Markownikoff, as authorized by the Council.

It was voted that educational institutions be allowed the same discount on sets of Journals as is given to dealers.

It was voted to close the contract with specifications for printing and distributing the Journal as agreed upon by the Committee on Contract and the Chemical Publishing Company. The president, the secretary, and the treasurer of the Society were directed to sign said contract in triplicate on behalf of the Society, and to accept the signature of Edward Hart to the contract on behalf of the Chemical Publishing Company. The contract was thereupon signed by both parties thereto, and acknowledgment of the same taken by notary public.

The proposition of Dr. Harwood Huntington to give a complete set of the *Berichte* in lieu of $100 in payment for life mem-

bership in the Society was accepted, and the treasurer was directed to transfer $100 from the general funds of the Society to the life membership fund on behalf of Dr. Huntington whenever the complete set of the *Berichte*, in good and acceptable condition, shall have been received by the librarian for this purpose.

The treasurer of the Society was directed to pay to the treasurer of the Washington Section the balance of funds to which that Section was entitled for dues paid by its members during the year 1900. It was voted also, that hereafter, in order that such sums may be available to any section, an application for said funds made in due form as prescribed in Section I of Article X of the constitution, must be received by the treasurer of the Society within the year in which said funds are payable.

A special appropriation not to exceed $25 was voted for binding a set of the Journal and Proceedings for the editor.

The Board then adjourned.

ALBERT C. HALE, *Secretary*

COUNCIL.

The following recommendations regarding obituary notices were approved by Council :

1. It is recommended that the secretary, upon being notified of the death of any member, shall insert a notice of the same of at most three or four lines in the next number of the Proceedings.

2. It is recommended that all obituary notices, except those provided for under Section I, shall be sent to the editor, and by him referred to at least two other members of the Committee on Papers and Publications. Their joint decision shall be final, in case the opinions of all coincide. In case of disagreement, however, the matter shall be referred to the president of the Society, whose decision shall be final.

3. It is recommended that obituary notices shall be printed in the Proceedings, the body of the Journal being reserved for strictly scientific matter.

The Council has elected the following named persons to fill the respective offices and committees mentioned :

For Secretary—Albert C. Hale.
For Treasurer—Albert P. Hallock.
For Librarian—E. G. Love.
For Editor—Edward Hart.
For Councilor (to fill balance of term of F. W. Clarke, president), W. B. Rising.

For Directors, to serve two years, beginning January 1, 1901—
C. A. Doremus, C. B. Dudley.

For Committee on Membership[1]—Wm. McMurtrie, C. L. Reese,
E. G. Love.

For Finance Committee[1]—J. H. Wainwright, Durand Woodman,
C. F. McKenna.

For Committee on Papers and Publications—Edward Hart, W. A.
Noyes, W. F. Hillebrand, E. F. Smith, J. H. Long, H. N.
Stokes, Wm. McMurtrie, H. P. Talbot, A. A. Noyes, H. W.
Wiley.

The following telegram was sent in the name of the Society on
the occasion of the celebration of the Fortieth Scientific Anni-
versary of the Russian Chemical Society, which took place
February 12, 1901.

"*Doctor N. Kijner, Polytechnic Museum, Moscow, Russia* :

The American Chemical Society sends greetings and congratu-
lations to Doctor Vladimir Markownikoff.

F. W. CLARKE, *President*,
ALBERT C. HALE, *Secretary*."

NAME PROPOSED FOR LIFE MEMBERSHIP.

Davis, H. J., 65 Wall St., N. Y. City.

NAME PROPOSED FOR MEMBERSHIP.

Adams, Arthur B., Takoma Park, D. C.
Allen, Eugene T., U. S. Geol. Survey, Washington, D. C.
Alpers, Wm. C., 45 W. 31st St., N. Y. City.
Arnold, Frank L., 247 Franklin St., Elizabethport, N. J.
Balch, Alfred W., 664 Huntington Ave., Boston, Mass.
Bartlett, Jane H., Amer. Glue Co., 417 Atlantic Ave., Boston,
Mass.
Base, Daniel, 309 N. Schroeder St., Baltimore, Md.
Bedford, A. C., 26 Broadway, N. Y. City.
Booth, Edward, 2214 Harrison St., Oakland, Cal.
Brinton, Clement S., Box 16, West Chester, Pa.
Browning, Charles, Jr., 1324 I St., Sacramento, Cal.
Case, Elisha W., 323 E. Williams St., Ann Arbor, Mich.
Chadwick, Walter M., 24 W. 3rd St., Bayonne, N. J.
Clamer, G. H., Ajax Metal Co., Philadelphia, Pa.
Clapp, Lowell T., 10 Park Sq., Boston, Mass.
Clark, Herbert A., 727 Washington Ave., Kansas City, Kan.

[1] *Note.*—Dr. Elwyn Walter and Mr. M. T. Bogert, who were nominated by the Council at
the annual meeting, were unable to serve, and their places were filled by Drs. McKenna
and Love.

Clark, Rufus W., Jr., 49 Erskine St., Detroit, Mich.
Colony, R. J., Cooper Institute, N. Y. City.
Fetterolf, Daniel D., 3310 Wallace St., Philadelphia, Pa.
Fraps, G. S., Raleigh, N. C.
Griswold, George G., care Globe Smelter, Denver, Colo.
Guiterman, Edward W., 125 Paulison Ave., Bayonne, N. J.
Hartzell, Mabel A., 1536 S. 18th St., Lincoln, Nebr.
Hawkins, J. D., Colo. Phila. Reduction Co., Colorado Springs, Colo.
Heath, W. P., Auburn and Courtland Sts., Atlanta, Ga.
Heckel, Frederic J., Bradford, Pa.
Hendee, Edward T., University Heights, N. Y. City.
Hitchcock, Romyn, 20 Broad St., N. Y. City.
Howard, Samuel F., Amherst, Mass.
Jungerich, Eldred E., 317 S. 11th St., Philadelphia, Pa.
Kauder, Ernst, care of Merck & Co., University Place, N. Y. City.
Kenrick, Edgar B., Winnipeg, Canada.
Klipstein, August, 122 Pearl St., N. Y. City.
Leavenworth, Wm. S., Ripon, Wis.
Libby, Geo. N., Room 54, 81 S. Clark St., Chicago, Ill.
Main, Wm., 299 Jefferson Ave., Brooklyn, N. Y.
Metz, Herman A., 122 Hudson St., N. Y. City.
Nation, Edmund C., 218 Nelson Ave., Peekskill, N. Y.
Painter, Jas. S., Pulaski, Va.
Paul, Arthur E., 12 S. Elizabeth St., Chicago, Ill.
Pierce, I. R., Repauno Chem. Co., Chester, Pa.
Remington, J. Percy, 36 Doughty St., Brooklyn, N. Y.
Riederer, Herman S., 145 W. 94th St., N. Y. City.
Roscow, Wm., 102 Central Ave., Pawtucket, R. I.
Ruhoff, O. E., Mineral Point, Wis.
Ryan, Leon A., 3607 Sansom St., Philadelphia, Pa.
Segerblom, Wilhelm, Phillips Exeter Acad., Exeter, N. H.
Siedler, George J., High Bridge, N. J.
Silliman, A. P., Hibbing, Minn.
Taylor, Alfred E., 641 Washington St., N. Y. City.
Turnbull, Frederick, 126–128 S. Front St., Philadelphia, Pa.
Waitt, Walter G., 58 Dwight St., Boston, Mass.
Wingate, Hamilton M., Lab., 20 Fort St., Auckland, N. Z.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Amberg, Arthur J., 1520 Melrose St., Chicago, Ill.
Hasslacher, Jacob, 100 William St., N. Y. City.
Hill, Arthur E., 118 Mt. Pleasant Ave., Newark, N. J.
Hood, Robert H., 737 Warren Ave., Chicago, Ill.
Mather, Stephen T., 2 N. La Salle St., Chicago, Ill.
McCarthy, J. H., Mountain Iron, Minn.

Murray, Robert H., 1911 W. 103rd St., Chicago, Ill.
Plant, Albert, 120 William St., N. Y. City.
Preston, J. F., Lowell, Mass.
Scott, Wm. F., 81 West St., Hyde Park, Mass.
Touzalin, Leslie A., 1600 W. Monroe St., Chicago, Ill.

NEW MEMBERS ELECTED FEBRUARY 20 1901.

Berolzheimer, D. D., 317 S. 18th St., Philadelphia.
Clark, Alfred N., Agricultural College, Mich.
Fitz-Gibbon, R., 77 John St., N. Y. City.
Lohmann, H. J., 90 Monticello Ave., Jersey City, N. J.
Stockwell, C. F., Bassett, Neb.

NEW MEMBERS ELECTED FEBRUARY 27, 1901.

Abbott, George A., M. T. High School, Indianapolis Ind.
Bacon, Raymond F., Vincennes Univ., Vincennes, Ind.
Barnard, Harry E., Naval Proving Ground, Indian Head, Md.
Benedict, C. Harry, Lake Linden, Mich.
Bowen, Ralph A., 163 Oliver St., Boston, Mass.
Brown, David S., Jr., 51st St. and North River, N. Y. City.
Cade, Marion L., 14 Clinton St., Cambridge, Mass.
Cady, Hamilton P., Lawrence, Kas.
Campbell, Eugene, University, Miss.
Chase, G. H., 6020 Greene St., Germantown, Philadelphia.
Craig, W. Dixon, Canada Iron Furnace Co., Midland, Ontario.
Cutter, Wm. D., 1208 Pacific St., Brooklyn, N. Y.
Ferris, Wm. S., 224 Murray St., Madison, Wis.
Fowler, Roy E., 428 Lake St., Madison, Wis.
Freas, Thomas B., Univ. of Chicago, Chicago, Ill.
Geis, John F., The Medical College of Indiana, Indianapolis, Ind.
Germer, J. W., 511 Lincoln Ave., Chicago, Ill.
Gillinder, James, Jr., 1509 Oxford St., Philadelphia, Pa.
Goody, Forest D., 701 S. Water St., Denver, Colo.
Hall, Roy D., 712 Langdon St., Madison, Wis.
Hantke, Ernst, 646 Broadway, Milwaukee, Wis.
Harris, Harry B., care Southern Cotton Oil Co., Savannah Ga.
Hendrixson, W. S., Iowa College, Grinnell, Iowa.
Holbrook, George M., 64th St. and Lexington Ave., Chicago, Ill.
Hunt, Caroline L., 1566 Ashland Ave., Evanston, Ill.
Kern, Edward F., 77 Lenox Ave., N. Y. City.
Mains, Elmer E., 415 Humboldt Ave., Detroit, Mich.
McCarthy, Maurice L., 1168 Massachusetts Ave., Cambridge, Mass.
Merzbacher, Aaron, Carpenter Steel Co., Reading, Pa.
Montgomery, John P., Univ. of Va., Charlottesville, Va.

Moore, Charles J., Charlottesville, Va.
Moore, Richard B., Univ. of Mo., Columbia, Mo.
Mosher, Willet H., Univ. of Buffalo, Buffalo, N. Y.
Porter, John L., Water Purification Station, New Orleans, La.
Pray, Charles P., Hempstead, N. Y.
Price, T. M., College Park, Md.
Smith, Alexander, Univ. of Chicago, Chicago, Ill.
Smith, Edward S., care Grasselli Chem. Co., East Chicago, Ind.
Smith, S. M., Elon College, N. C.
Titus, Winifred, 202 Langdon St., Madison, Wis.
Walters, Edward P., 22 Everett Ave., Dorchester, Mass.
Walworth, Joseph E., Lawrence, Mass.
Wills, J. Lainson, 133 Midwood St., Flatbush, Brooklyn, N. Y.
Wright, Frank, 2421 Dearborn St., Chicago, Ill.
Youtz, L. A., 1272 Amsterdam Ave., N. Y. City.
Ziegler, Howard, 526 Penn St., Reading, Pa.

ASSOCIATES ELECTED FEBRUARY 27, 1901.

Bloom, Warren E., 44 Montgomery St , Jersey City, N. J.
Driscoll, J., 71 Centre St., Roxbury, Mass.
Langmuir, Irving, 185 W. 135th St., N. Y. City.

NEW MEMBERS ELECTED MARCH 13, 1901.

Aldrich, Thomas B., 284 Pennsylvania Ave., Detroit, Mich.
Arnold, Charles E., Sidney, C. B., Canada.
Barker, Elliott R., Berlin, N. H.
Barrows, Ernest R., Albany Chemical Co., Albany, N. Y.
Fritchle, Oliver P., 1734 Arapahoe St., Denver, Colo.
Goessmann, Charles I., 728 Main St., Worcester, Mass.
Hart, Walter H., 2010 Wallace St., Philadelphia, Pa.
Hauser, F. C., Jr., 6th and Main Sts., Covington, Ky.
Kohl, Herbert C., Craigsville, Va.
McDonnell, Curtis C., Clemson College, S. C.
McFarland, David F., State Univ., Lawrence, Kans.
Morre, G. J., Jr., 271 W. 22d St., N. Y. City.
Page, Logan W., 2019 O St., Washington, D. C.
Ryland, Garnett, Orono, Me.
Schlisinger, Bart E., Warren St., Brookline, Mass.
Thomas, George E., 1513 N. Gratz St., Philadelphia, Pa.
von Isakovics, Alois, 457 E. 121st St., N. Y. City.
Watkins, James B., 1424 Aisquith St., Baltimore, Md.
Wilkins, Albert D., 8 Sprague Ave., Bellevue P. O. Station, Allegheny, Pa.
Young, J. Bertram, 532 Franklin St., Reading, Pa.
Zeiss, William, 54 Lawrence Ave., Detroit, Mich.

ASSOCIATES ELECTED MARCH 13, 1901.

Baldwin, Wareham S., 522 Monroe St., Ann Arbor, Mich.
Ellett, T. S., 3767 Ellis Ave., Chicago, Ill.
Law, Leroy M., 310 9th St., N. E., Washington, D. C.
McKnight, J. Renwick, Wm. Cramp & Sons, York and
Thompson Sts., Philadelphia, Pa.
Sammet, George V., 73 Sheridan St., ·Boston, Mass.
Sheiry, Dillon, 132 F St., N. E., Washington, D. C.
Smith, Roger G., 314 A St., N. E., Washington, D. C.

CHANGES OF ADDRESS.

Ackerman, Franz W., 54 Livingston St., Brooklyn, N. Y.
Anderson, Duncan, Jr., Radnor Forges, P. Q., Canada.
Elworthy, H. S., 153 The Grove, Denmark Hill, S. E. London,
Eng.
Evans, W. L., Box 371, Colorado Springs, Colo.
Felt, W. W., 9431 Longwood Ave., Chicago, Ill.
Hamilton, Louis P., Hornitos, Cal.
Hoffman, P. C., Box 466, Savannah, Ga.
Lamborn, Leebert L., care Maple City Soap Co., Monmouth,
Ill.
Lazell, E. W., 1109 Stephen Girard Bldg., Philadelphia, Pa.
Mallory, J. Halsey, 919 Anstell Bldg., Atlanta, Ga.
McDowell, A. H., Helper, Utah.
Nathan, Albert F., Jr., U. S. Patent Office, Washington, D. C.
Neilson, Thomas, Redding, Shasta Co., Cal.
Perkins, T. S., care Cal. Tartar Works, 123 California St.,
San Francisco, Cal.
Sanborn, E. R., West Middlesex, Pa.
Schuyler, E. H., High School, Erie, Pa.
Shepard, C. H., Union Iron Works, Chem. Lab., Potrero, Cal.
Simons, F. D., The Essex, 1422 N St., Washington, D. C.
Smiley, W. P., 145 Parkview Ave., Buffalo, N. Y.
Veitch, F. P., Div. of Soils, U. S. Dept. of Agr., Washington,
D. C.
Voorhees, Gerald E., 1025 Spruce St., Philadelphia, Pa.
Watson, Henry E. G., 5333 Wayne Ave., Germantown, Pa.
Wing, Herbert H., 326 Richmond Terrace, New Brighton,
S. I., N. Y.

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DECEASED MEMBERS.

Mr. Hermann A. Loos, of New York City, member of the
Society since 1898, died July 17, 1900.

Mr. Allan Wells, of Pittsburg, Pa., member of the Society
since 1900, died October 15, 1900.

Major C. Chauncey Parsons, of Brooklyn, N. Y., member of the Society since 1894, and secretary of the *Committee on Patent and Related Legislation* since its appointment, died January 16, 1901.

Mr. Edward L. Smith, of Worcester, Mass., member of the Society since 1893, died February 19, 1901.

Professor Lawrence S. Williams, of Chicago, Ill., member of the Society since 1899, died February 19, 1901.

MEETINGS OF THE SECTIONS.

NEW YORK SECTION.

The February meeting was held on Friday evening, February 8th, at the Chemists' Club, Dr. C. A. Doremus presiding, and sixty-five members present.

The minutes of the January meeting were read and accepted as read.

The following papers were read:

"The Chemistry of Materials used in Perfumery and Kindred Arts," by T. C. Stearns.

"Decomposition of the Chlorides of the Alkali Metals by Sulphuric Acid," with exhibition of crystals, by C. W. Volney.

"Metallic Soaps from Linseed Oil : An Investigation of Their Solubilities in Certain of the Hydrocarbons," by H. T. Vulté and Harriet W. Gibson.

a. "On the Heat of Combustion as a Factor in the Analytical Examination of Oils," *b.* "The Heats of Combustion of Some Commercial Oils," by H. C. Sherman and J. F. Snell.

During the discussion of Dr. Stearns' paper, President F. W. Clarke and Past Presidents Dudley and McMurtrie arrived and were invited to seats on the platform.

Dr. Volney exhibited crystals which he considered as poly-sulphates. Prof. Bogert and others thought they were acid sulphates with sulphuric acid of crystallization, and that even their thermal behavior was in favor of this view.

In the discussion of the paper read by Dr. Vulté, Prof. Sabin said that a great many of the driers in use were made from rosin and contained no linseed soaps at all. Dr. Dudley said he knew of no subject needing more study than the chemistry of the dry-

ing of oil, and that a great deal of time had been spent on it in his laboratory. He said that shellac was a substance used in driers which he was surprised not to find mentioned in the paper read. He found that oil driers used in excess retard drying, but that gum shellac driers could be used in all proportions and drying would occur approximately in proportion to the drier used. He had also found that a lead and manganese drier could be prepared which would induce drying of linseed oil in two hours.

In the discussion of the paper presented by Messrs. Sherman and Snell, it was shown that in the case of a drying oil exposure to the air produced a reduction in the heat of combustion which may amount to 10 per cent., whereas lard oil with the same exposure lost only 1 per cent. of its heat of combustion.

To ignite the oil in the bomb calorimeter it was found satisfactory to absorb it on asbestos wool, whereby the use of any special igniting substance with its consequent introduction of a troublesome error, was entirely obviated.

The chair announced that a new set of by-laws had been drawn up by the Executive Committee, and would be presented for adoption.

They were then read by the secretary and unanimously adopted as follows:

By-Laws for Governing the New York Section of the American Chemical Society.

First: All members of the American Chemical Society residing in New York City, and within fifty miles of the City Hall of that city, shall be members of the Section.

Second: The officers of the Section shall consist of a Chairman, Vice-Chairman, and also of a Secretary and Treasurer combined in one person; an Executive Committee to consist of the above officers and three additional members of the Section.

Third: The officers shall be elected by ballot, and installed at the meeting which shall be held annually on the first Friday after the first Monday in June.

Fourth: The Section shall hold nine meetings a year, one upon the first Friday after the first Monday of each month, excepting July, August, and September. Special meetings may be called at the discretion and by the order of the Executive Committee.

Fifth: No papers may be read in open meeting until they have been approved by the Executive Committee.

Sixth: All papers read at the meetings of the Section must be

submitted to the Executive Committee before being sent to the Editor of the Journal.

Seventh : Papers intended for publication shall be delivered to the secretary at the close of the meeting at which they have been read.

Eighth : The treasurer shall submit all bills to the Executive Committee before payment, shall annually report to the Executive Committee, and his report and accounts shall be examined and audited by a committee of two, to be appointed by the Chairman of the Section.

Ninth : Order of business : Reading of Minutes, Report of Officers and Executive Committee, Reading of Papers, Special Committee Reports, Miscellaneous Business.

Tenth : The Section shall be otherwise governed and controlled by the Constitution of the Society.

On motion, E. H. Miller was nominated and elected as member of the Executive Committee to take the place of Prof. Bogert, Vice-Chairman, as required by the by-laws.

The meeting was then adjourned.

DURAND WOODMAN, *Secretary.*

WASHINGTON SECTION.

The 124th regular meeting was held February 14. Dr. H. Carrington Bolton, the retiring president, addressed the Society on the subject '' Physics and Faith.''

The following papers were then presented : '' The Solubility of Gypsum in Aqueous Solution of Sodium Chloride,'' by F. K. Cameron.

This paper was a description of the continuation of investigations along this line previously reported by the author. It was found that the solubility curve presented a maximum point even when calculated on the basis of a given mass of solvent instead of a given volume of solution. A discussion, together with the results of experiments, was given on the nature of the hydrate of calcium sulphate in the solid phase in contact with certain solutions. A theoretical discussion of the results was presented, and some practical applications pointed out.

'' Equilibrium between Carbonates and Bicarbonates in Aqueous Solution,'' by F. K. Cameron and J. L. Briggs.

The curves showing the distribution of the base between the two salts for solutions in equilibrium with ordinary air were shown. For solutions of the salts of sodium, potassium, or

magnesium, as infinite dilution is approached the bases are all combined as hydrogen carbonates. As the total concentration increases, the percentage of base combined as normal carbonate increases rapidly to a certain point, then asymptotically and as the solutions approach high concentration there is again a falling off, showing the existence of maximum points on the curves. Solutions of calcium salt contain so little normal carbonate when in equilibrium with air, that practically they may be considered as containing only the hydrogen carbonate. With rise of temperature, in all cases, there is an increase in the proportion of normal carbonate in the solution, and at 100° C. all the base is combined as normal carbonate for practically all concentrations. A theoretical discussion accompanied the paper, and practical applications of the results were pointed out.

L. S. MUNSON, *Secretary.*

CINCINNATI SECTION.

The 77th regular meeting was held in the Chemical Lecture Room, Hanna Hall, University of Cincinnati, on Monday evening, October 15, 1900. Miss Hannah L. Wessling, first vice-president, presided in the absence of the president. Dr. A. T. Lincoln presented the paper of the evening on "Physical Reactions and the Mass Law."

The 78th regular meeting was held on Thursday evening, November 15, 1900. Officers of the Section for 1901 were nominated, and Dr. Thomas Evans was elected representative in the council. Prof. O. W. Martin presented a paper on "The Manufacture of Carborundum at Niagara Falls," and illustrated it with a number of lantern slide views.

The 79th regular meeting was held on Saturday evening, December 15, 1900, at the usual place of meeting at the university. The following officers were elected for the year 1901 : President, Wm. H. Crane; first vice-president, Robert W. Hochstetter; second vice-president, B. M. Pilhashy; secretary, Frank I. Shepherd; treasurer, Henry B. Foote; Executive Committee, Otto Dieckmann, Cora Morton, and R. W. Proctor. Two very interesting papers were presented. One by Dr. J. H. Kastle, on "The Nature of the Enzymes," and the other by Dr. H. M. Gordin, on "The Alkalimetric Factors of Some Alkaloids."

On Saturday, January 19, 1901, the Section celebrated its 10th anniversary. In the afternoon the members and guests were conducted through the Rookwood Pottery by its superintendent, Mr. Stanley G. Burt. In the evening a German supper and commers was had at the Hotel Sterling.

The 81st regular meeting was held on Friday evening, February 15, 1901. In the absence of the secretary, Dr. S. Waldbott occupied his position for the evening. Dr. H. E. Newman read a paper on " Atomic Divisibility," and Dr. Alfred Springer presented a brief paper on " The Purification of River Water by Means of Caustic Alkalis."

At the March meeting, Thursday evening the 14th, papers were presented by Dr. H. M. Gordin, on " Method for the Assay of Drugs," and by Dr. Alfred Springer, on " Things Unscientific."

FRANK I. SHEPHERD, *Secretary.*

Proceedings.

TWENTY-FIFTH ANNIVERSARY OF THE AMERI-
CAN CHEMICAL SOCIETY.

Twenty-Third General Meeting.

The twenty-fifth anniversary of the organization of the Ameri-
can Chemical Society was celebrated by a general meeting of the
Society, held in New York City, Friday and Saturday, April 12
and 13, 1901. The sessions were held in the assembly hall of
the Chemists' Club, 108 W. 55th Street, by special invitation of
the trustees of the club. The rooms of the club were the head-
quarters for the anniversary celebration, and the privileges of the
club were extended to all the visiting chemists.

During the forenoon of Friday, April 12th, the Registration
Committee was in attendance at the Chemists' Club, where the
visiting chemists were informally received and welcomed. At 1
P.M. on Friday, luncheon was served at the club, through the
courtesy of the New York Section of the Society.

The first session of the meeting was called to order at 2.40 P.M.
by Dr. C. A. Doremus, chairman of the New York Section, who
welcomed the chemists on behalf of the local section, and out-
lined the general plan for the celebration. Dr. Doremus then
introduced Mr. T. J. Parker, president of the Chemists' Club,
who addressed some words of welcome on behalf of the club.
President F. W. Clarke responded on behalf of the Ameri-
can Chemical Society, expressing the thanks of the visiting
chemists for their welcome, and making a few remarks on the
condition and prospects of the Society.

The minutes of the last general meeting of the Society were
approved as recorded by the secretary. The secretary then read
several communications received relative to the occasion, includ-
ing a large number of replies from invited guests, and a telegram
of congratulation from the Chicago Section of the Society.

The following papers were then presented : " Chemical Socie-
ties of the XIX Century," by H. Carrington Bolton. Read by
C. A. Doremus. " Historical Sketch of the American Chemical
Society," by Albert C. Hale. " Organization and Development
of the Chemical Section of the American Association for the
Advancement of Science," by Marcus Benjamin. Read by the
secretary. " Progress in Organic Chemistry during the Past
Twenty-five Years," by W. A. Noyes. Presented in abstract by
Charles Baskerville.

Dr. Baskerville also presented the following papers which were
read by title : " Aims and Opportunities Offered in Physical
Chemistry in America," by Louis Kahlenberg. " Improved
Teaching in Technical Chemistry and Results Accomplished by
the Application of Chemistry to the Arts in America since the
Founding of the American Chemical Society," by Charles E.
Munroe. " Progress of Teaching Chemistry in the Schools
Since the Founding of the American. Chemical Society," by
Rufus P. Williams.

Dr. Baskerville then made a report of progress, summing up
the work already accomplished by the Census Committee.

It was voted that the various reports that had been presented
be referred back to their committees for coordination, completion,
and subsequent reference to the Committee on Papers and
Publications.

The secretary presented to the society the names of the follow-
ing persons as nominees for election to honorary membership,
stating that the requirements of the constitution in reference
thereto had been complied with, and moving that the persons so
presented be elected as honorary members. The motion was duly
seconded and unanimously adopted. The list of persons so elected
includes : Professor William Ramsay, University College, London,
Eng.; Professor Doctor Emil Fischer, Berlin, Germany ; Professor
Doctor Adolph von Baeyer, Munich, Germany ; Professor
Doctor George Lunge, Zurich, Switzerland ; Sir Henry E.
Roscoe, University of London, Eng.

After a few announcements, the afternoon session was
adjourned.

At the close of the afternoon session, a meeting of the council
of the Society was held in the assembly hall of the club. After
the consideration of a number of subjects which were presented,

the council adjourned for final deliberation upon them at 9 A.M. the next day, in conformity with the official announcement of the meeting which had been sent to the councilors.

EVENING SESSION.

The evening session was called to order in the assembly hall of the Chemists' Club, at 8.45 P.M. by President Clarke. Addresses were delivered as follows : "The Dignity of Chemistry," by H. W. Wiley. "Formation of the American Chemical Society," by C. F. Chandler. After the addresses, on motion of Dr. Morley, the thanks of the Society were unanimously voted to the New York Section of the Society and the local Committee of Arrange ments ; to the trustees of the Chemists' Club for their courtesies and the use of their rooms ; to the chairman of the New York Section and the president of the Chemists' Club for their cordial words of welcome ; to the officers and managers of the various institu tions and works opened for inspection to the visiting chemists.

After some announcements, the evening session was adjourned.

At the close of the evening session, refreshments were served by the New York Section of the Society to the chemists and their friends who remained to enjoy a brief social occasion.

SATURDAY, APRIL 13TH.

The day was spent in the enjoyment of the various visits and excursions arranged for by the local committee, and in the eve-ning a subscription dinner was enjoyed at the Hotel Savoy, 59th Street and Fifth Avenue.

COUNCIL.

The council of the American Chemical Society met in the assembly hall of the Chemists' Club, New York City, on Friday, April 12, 1901. The meeting was called to order by the president of the Society at 4.50 P.M. There were present Messrs. Clarke, McMurtrie, Mallet, Baskerville, Hale, Morley, Chandler, Dore-mus, A. A. Noyes, Talbot, Remsen, and Stone.

The former minutes of the council were approved as recorded by the secretary

The council voted to approve the nominations to membership made up to the close of the anniversary meeting and directed the secretary to declare such nominees elected whenever all other requirements of the constitution should be met.

It was voted to authorize the librarian to sell sixteen volumes of back numbers of the Journal to Professor Neher at the regular specified price.

The librarian was also authorized and directed in his discretion to purchase such back numbers of the Journal as are offered for sale and as he might deem desirable and to keep them in stock.

The librarian and treasurer were constituted a committee to arrange for insurance of the stock of Journals kept at the Chemists' Club.

The council voted to suggest to the directors that they appropriate from funds not otherwise appropriated, the sum of $75 to defray the expense of storage of the back numbers of the Journal which are kept at the Chemists' Club. The librarian was authorized to collect the cost of transportation of back numbers of the Journal to delinquents in payment of dues.

The action of the directors with reference to accepting a set of the *Berichte* in lieu of $100 as payment for life membership for Harwood Huntington was approved. It was voted that when the council adjourns it adjourns to meet at the Chemists' Club to-morrow morning at 9 o'clock, and that the secretary be instructed to have his report of this meeting ready for presentation at that time:

The council then adjourned.

ALBERT C. HALE, *Secretary*.

ADJOURNED MEETING OF THE COUNCIL.

The adjourned meeting of the council of the American Chemical Society was held at the Chemists' Club, Saturday, April 13, 1901.

The meeting was called to order by President Clarke at 9 A.M.

There were present Messrs. Clarke, Wiley, Hart, Doremus, Chandler, Hale, Mallet, Remsen, E. E. Smith, McMurtrie, Talbot, A. A. Noyes, Caldwell, Baskerville, and Stone.

The minutes of the previous meeting were approved as recorded by the secretary.

The action of the council at the meeting of April 12th was approved and adopted.

It was voted that the Committee on Papers and Publications be directed to publish the proceedings, papers, and all matter of report pertaining to the anniversary meeting in a separate volume.

It was also voted that the directors be authorized to appropriate the sum of $500, or so much thereof as may be necessary, from funds not otherwise appropriated, to cover the expense of completing and publishing the proceedings of the twenty-fifth anniversary.

Dr. Hart presented the following report from the Committee on Papers and Publications: "The Committee on Papers and Publications met at the Chemists' Club at 7.15 P.M., April 12, 1901. Doctors Hart, McMurtrie, Wiley, Talbot, and A. A. Noyes were present.

Dr. A. A. Noyes announced that it would probably be impossible to continue after the end of the present year the "Review of American Chemical Research" as a contribution from the Massachusetts Institute of Technology, owing to the fact that many of the reviewers who have now been engaged in the work for several years have come to feel that it is a serious burden and desire to be relieved of the work.

Dr. Hart announced that he had been unsuccessful in engaging an editor to take charge of the plan of preparing abstracts of chemical work in general, although he has approached three members of the Society.

On motion of Dr. Wiley and second of Dr. McMurtrie, it was voted that it is the sense of the committee that it is impracticable to carry out the spirit of the resolution adopted at the Chicago Meeting in regard to the preparation of abstracts of chemical work in general, but that it is advisable to continue and make more complete the ' Review of American Chemical Research.' "

On motion of Dr. Hale, the report was accepted and its recommendation adopted.

It was voted that the action of the council at the meeting in Chicago covering the preparation of abstracts be and is hereby repealed, and that the directors be and they are hereby authorized to repeal the appropriation of monies to carry on the work designated.

It was also voted that the sum of $100, or so much thereof as may be necessary, be and is hereby appropriated, from funds not otherwise appropriated, to be used by the Committee on Papers and Publications in carrying into effect the provisions of the report of said committee as adopted by the council.

The council then adjourned. ALBERT C. HALE, *Secretary.*

BOARD OF DIRECTORS.

The meeting was called to order by the president of the Society at 10.10 A.M., Saturday, April 13, 1901. There were present Messrs. Clarke, Chandler, E. E. Smith, and Hale.

The minutes of the previous meetings, up to date, were adopted as recorded by the secretary.

Upon motion of Dr. McMurtrie, it was resolved that the sum of $75, or as much thereof as may be necessary, be and is hereby appropriated from funds not otherwise appropriated, to defray the expense of storage of the back numbers of the Journal which are kept in the building of the Chemists' Club.

It was also voted that the sum of $500, or as much thereof as may be necessary, be and is hereby appropriated, from funds not otherwise appropriated, to cover the expense of compiling and publishing the proceedings of the twenty-fifth anniversary of the Society.

It was voted that the sum of $100, or as much thereof as may be necessary, be and is hereby appropriated, from funds not otherwise appropriated, to be used by the Committee on Papers and Publications in carrying into effect the provisions of the report of said committee presented to, and adopted by, the Council this day.

It was voted that the librarian be authorized to sell to Professor Neher sixteen volumes of the back numbers of the Journal.

It was voted that the librarian be and is hereby authorized and directed in his discretion to purchase such back numbers of the Journal as are offered for sale and as may seem to him desirable, and to keep them in stock.

It was voted that the librarian and treasurer be constituted a committee to arrange for the insurance of the stock of Journals kept in the building of the Chemists' Club.

It was voted that the librarian be and is hereby authorized to collect the cost of transportation of back numbers of the Journal to delinquent members on payment of their dues.

It was also voted that since the action of the council at the meeting in Chicago covering the preparation of abstracts has been repealed, the directors hereby repeal the appropriation of monies to carry on the work designated.

The following resolution was unanimously adopted :

Resolved, " That the treasurer of this Society be, and he hereby

is authorized to receive and give receipts for all money due and payable to this Society from any source whatever, and to endorse checks and warrants in its name and on its behalf, and full discharge for the same to give."

The directors then adjourned.

ALBERT C. HALE, *Secretary*.

NAMES PROPOSED FOR MEMBERSHIP.

Arndt, Frederick J. P., 226 E. 35th St., N. Y. City.

Breidenbaugh, Edward S., Pennsylvania College, Gettysburg, Pa.

Broshears, John W., 27-34 Rialto Bldg., Chicago, Ill.

Clement, D. H., Butte, Mont.

Clevenger, Galen H., Rapid City, S. D.

Dreyfus, Wm., 208 E. 52nd St., N. Y. City.

Falding, Frederic J., Exchange Court, 52 Broadway, N. Y. City.

Friedburg, L. H., 292 Van Buren St., Brooklyn, N. Y.

Frusher, Tom, 87 Nassau St., N. Y. City.

Fudge, Thomas, 43 W. 27th St., Bayonne, N. J.

Fuerst, W. F., 2 Stone St., N. Y. City.

Gass, James K., 717 Spruce St., Philadelphia, Pa.

Goldsmith, B. B., 19 E. 74th St., N. Y. City.

Gordon, Frederick T., Navy Yard, Philadelphia, Pa.

Harvey, Edward F., St. Johns, Newfoundland.

Hopkins, B. Smith, 358 W. 118th St., N. Y. City.

Johnson, Thomas H., 28 Hinchman Ave., Dover, N. J.

Krebs, August S., Wilmington, Del.

Lewis, W. B., care of Sargent Co., Chicago Heights, Ill.

von der Linde, Harold T. G., 101 Tyndall Ave., Toronto, Canada.

Lyons, Albert B., 72 Brainard St., Detroit, Mich.

Mark, Kenneth L., 109 Irving St., Cambridge, Mass.

Mosesom, Moses, 1813 Lexington Ave, N. Y. City.

Novarine, John L., 101 Henry St., Brooklyn, N. Y.

Rauchfuss, Eugene J., 161 E. Broadway, N. Y. City.

Ronan, Gerald P., Butte, Mont.

Ryan, Irenaeus, Barbar Asphalt Co., Long Island City, N. Y.

Schultz, Carl Rudolph, 440 First Ave., N. Y. City.

Sickels, Ivin, 17 Lexington Ave., N. Y. City.

Sims, Arthur A., Univ. of Neb., Lincoln, Neb.

Stevenson, M. R., Tyrone, Pa.

Stoddart, Charles W., 526 S. Broadway, Yonkers, N. Y.

Thies, E. E., 125 Park Ave., Hoboken, N. J.

Thompson, Gustav W., Adams and Water Sts., Brooklyn, N. Y.

Tiemann, Hugh P., 125 W. 43d St., N. Y. City.

Timme, Walter, 102 W. 85th St., N. Y. City.
Wirth, Adam, 1004 Aline St., New Orleans, La.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Davis, R. O. E., Chapel Hill, N. C.
Klugh, B. G., Chapel Hill, N. C.
Marsh, L. Stanley, Ann Arbor, Mich.
Miller, Raymond M., 152 E. 20th St., N. Y. City.
Palmenberg, Oscar W., 107 W. 70th St., N. Y. City.
Rand, Charles L., 929 Lafayette Ave., Brooklyn, N. Y.
Rindskopf, Herbert A., 701 Madison St., Brooklyn, N. Y.
Saxe, Sigmond, 108 Fulton St., N. Y. City.
Shipman, Wm. W., 20 2nd St., West Manchester, N. H.
Silverman, Alexander, Western Univ., Allegheny, Pa.
Steinmuller, Wm., Mineral Point Zinc Co., Mineral Point, Wis.
Strahorn, Arthur T., Univ. of Neb., Lincoln, Neb.

NEW MEMBERS ELECTED APRIL 4, 1901.

Atkinson, James P., 36 Washington Sq., W., N. Y. City.
Axson, Edward W., Mannie, Tenn.
Bermingham, John, Jr., Pinole, Contra Costa Co., Calif.
Eldred, Frank R., Butte, Mont.
Gordin, Harry M., 503 E. 3rd St., Cincinnati, O.
Little, C. A., Box 517, Elyria, O.
Rust, Robert R., Bound Brook, N. J.
Smith, Theodore E., 221 W. 83rd St., N. Y. City.
Twieg, Wm. C., Pinole, Contra Costa Co., Calif.

LIFE MEMBER ELECTED APRIL 18, 1901.

Davis, H. J., 65 Wall St., N. Y. City.

NEW MEMBERS ELECTED APRIL 18, 1901.

Adams, Arthur B., Takoma Park, D. C.
Allen, Eugene T., U. S. Geol. Survey, Washington, D. C.
Alpers, Wm. C., 45 W. 31st St., N. Y. City.
Arnold, Frank L., 247 Franklin St., Elizabethport, N. J.
Balch, Alfred W., 664 Huntington Ave., Boston, Mass.
artlett, Jane H., Amer. Glue Co., 417 Atlantic Ave., Boston.
ase, Daniel, 329 N. Schroeder St., Baltimore, Md.
Bedford, A. C., 26 Broadway, N. Y. City.
Booth, Edward, 2214 Harrison St., Oakland, Cal.
Brinton, Clement S., Box 16, West Chester, Pa.
Browning, Charles, Jr., 1324 I St., Sacramento, Cal.
Case, Elisha W., 323 E. Williams St., Ann Arbor, Mich.
Chadwick, Walter M., 24 W. 3rd St., Bayonne, N. J.
Clamer, G. H., Ajax Metal Co., Philadelphia, Pa.
Clapp, Lowell T., 10 Park Sq., Boston, Mass.

Clark, Herbert A., 727 Washington Ave., Kansas City, Kans.
Clark, Rufus W., Jr., 49 Erskine St., Detroit, Mich.
Colony, R. J., Cooper Institute, N. Y. City.
Fetterolf, Daniel D., 3310 Wallace St., Philadelphia, Pa.
Fraps, G. S., Raleigh, N. C.
Griswold, George G., Globe Smelter, Denver, Colo.
Guiterman, Edward W., 125 Paulison Ave., Bayonne, N. J.
Hartzell, Mabel A., 1536 S. 18th St., Lincoln, Neb.
Hawkins, J. D.,.Colo. Phila. Reduction Co., Colorado Springs,
Colo.
Heath, W. P., Auburn and Courtland Sts., Atlanta, Ga.
Heckel, Frederic J., Bradford, Pa.
Hendee, Edward T., University Heights, N. Y. City.
Hitchcock, Romyn, 20 Broad St., N. Y. City.
Howard, Samuel F., Amherst, Mass.
Jungerich, Eldred E., 317 S. 11th St., Philadelphia, Pa.
Kauder, Ernst, care Merck & Co., University Place, N. Y. City.
Kenrick, Edgar B., Winnipeg, Canada.
Klipstein, August, 122 Pearl St., N. Y. City.
Leavenworth, Wm. S., Ripon, Wis.
Libby, George N., Room 54, 81 S. Clark St., Chicago, Ill.
Main, Wm., 299 Jefferson Ave., Brooklyn, N. Y.
Metz, Herman A., 122 Hudson St., N. Y. City.
Nation, Edmund C., 218 Nelson Ave., Peekskill, N. Y.
Painter, Jas. S., Pulaski, Va.
Paul, Arthur E., 12 S. Elizabeth St., Chicago, Ill.
Pierce, I. R., Repauno Chem. Co., Chester, Pa.
Remington, J. Percy, 36 Doughty St., Brooklyn, N. Y.
Riederer, Herman S., 145 W. 94th St., N. Y. City.
Roscow, Wm., 102 Central Ave., Pawtucket, R. I.
Ruhoff, O. E., Mineral Point, Wis.
Ryan, Leon A., 3607 Sansom St., Philadelphia, Pa.
Segerblom, Wilhelm, Phillips Exeter Acad., Exeter, N. H.
Siedler, George J., High Bridge, N. J.
Silliman, A. P., Hibbing, Minn.
Taylor, Alfred E., 641 Washington St., N. Y. City.
Turnbull, Frederick, 126–128 S. Front St., Philadelphia, Pa.
Waitt, Walter G., 58 Dwight St., Boston, Mass.
Wingate, Hamilton M., Laboratory, 20 Fort St., Auckland,
N. Z.

ASSOCIATES ELECTED APRIL 18, 1901.

Amberg, Arthur J., 1520 Melrose St., Chicago.
Hasslacher, Jacob, 100 William St., N. Y. City.
Hill, Arthur E., 118 Mt. Pleasant Ave., Newark, N. J.
Hood, Robert H., 737 Warren Ave., Chicago.
Mather, Stephen T., 2 N. La Salle St., Chicago.
McCarthy, J. H., Mountain Iron, Minn.

Murray, Robert H., 1911 W. 103rd St., Chicago.
Plant, Albert, 120 William St., N. Y. City.
Preston, J. F., Lowell, Mass.
Scott, Wm. F., 81 West St., Hyde Park, Mass.
Touzalin, Leslie A., 1600 W. Monroe St., Chicago.

CHANGES OF ADDRESS.

Appleby, W. R., Room 24, Pillsbury Hall, State Univ., Minneapolis, Minn.
Austen, Peter T., 80 Broad St., N. Y. City.
Baxter, Wm. T., 254 New York St., Aurora, Ill.
Bellam, Henry L., Wadsworth, Nev.
Bosart, L. W., Jr., Care Mrs. E. M. Durfee, 316 E. 60th St., Chicago, Ill.
Bragg, E. B., 1116 Michigan Ave., Evanston, Ill.
Chamberlain, Joseph S., Johns Hopkins Univ., Baltimore, Md.
Colley, Bernard T., Am. S. & R. Co., Argentine, Kans.
Evans, Ernest, 407 N. 5th St., Steubenville, O.
Fite, C. C., 102 W. 93d St., N. Y. City.
Frost, Howard V., 3958 Drexel Boulevard, Chicago, Ill.
Hale, Albert C., 352-A Hancock St., Brooklyn, N. Y.
Hulett, Geo. A., 1218 South University Ave., Ann Arbor, Mich.
Leach, Mary F., 202 S. Thayer St., Ann Arbor, Mich.
Mahon, R. W., Baggaley, Pa.
Merrill, Martin, 915 Fillmore St., San Francisco, Cal.
Poole, Herman, Watertown, Mass.
J. A. Schloss, Apartado 65, Monterey, Mexico.
Sovereign, Clarence L., Rockford, Ill.
Terne, Brnno, care The Union Abettoire Co., Baltimore, Md.
Weed, Henry T., 80 Livingston St., Brooklyn, N. Y.
Wilson, E. F., 224 South Eighth St., Philadelphia, Pa.
Wilson, H. T., 206 E. Armstrong Ave., Peoria, Ill.

DECEASED MEMBERS.

Dr. John A. Myers, of New York City, member of the Society since 1893, died April 8, 1901.

Dr. William J. Youmans, of New York City, member of the Society since 1876, died April 10, 1901.

MEETINGS OF THE SECTIONS.

MICHIGAN SECTION.

The Michigan Section met in the convention hall of the Russell House, Detroit, on Friday evening, April 26th, at eight o'clock. About sixty members and visitors were in attendance.

The following papers were presented : " Chemical Architec-

ture," by Dr. J. M. Francis ; "Comparison of Methods for Direct Analysis of Beets," by Mr. David L. Davoll, Jr.; " Trivalent Carbon," by Dr. M. Gomberg.

Previous to the meeting there was an informal dinner at the Russell House, with twenty-six present. A communication from the Michigan Academy of Science was read, proposing an affiliation of all the scientific organizations of the state. The president of the Section, Professor Freer, was appointed to represent the Section at a conference of societies interested.

ALFRED H. WHITE, *Secretary*.

CHICAGO SECTION.

The thirty-eighth meeting of the Chicago Section was held Monday evening, February 18th, at the Sherman House.

The paper of the evening was given by Prof. C. F. Mabery, of the Case School of Applied Science, Cleveland, O.

Prof. Mabery gave a very intersting talk on some recent work on the constituents of petroleum and the general condition of the oil industry at the present day.

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Monday evening, February 25th, Prof. Ira Remsen was the guest of the Chicago Section, at an informal dinner at the Sherman House.

Prof. Remsen gave a talk, after the dinner, on modern chemistry and some of its problems. F. B. DAINS, *Secretary*.

WASHINGTON SECTION.

The 125th regular meeting of the Washington Section was held March 14th. The following papers were presented :

"Notes on a New Indicator," by E. G. Runyan. In this paper were presented results on the determination of total acidity in both white and colored wines, using as an indicator an alcoholic solution of malachite green and commercial rosolic acid or corralin. For comparison, results obtained on the same samples with phenolphthalein and litmus were also presented. The data given seemed to be favorable to the use of the corralin-malachite indicator in titrating wines and similar colored products.

"The Action of Saccharin on Sugars and Other Carbohydrates," by L. M. Tolman. The author stated that saccharin was being sold as a substitute for sugar, and that it was sometimes found mixed with cane-sugar. The best method of determining

the saccharin present is the Reid method, by which the saccharin is hydrolyzed to the acid ammonium salt of sulphobenzoic acid, and the ammonia determined by distillation. The benzol-sulphimide was found to be a strong hydrolyzing agent, readily inverting cane-sugar. With cane-sugar, the inversion was as complete as by the official method, and, upon heating for a long time, there was no destruction of sugar. Lactose and dextrin were not affected by the sulphinide, a fact that may be used in the determination of cane-sugar in the presence of milk-sugar or dextrin, or both.

"The Nature and Function of Soil Solutions," by F. K. Cameron.

"Potassium Permanganate as a Chemical Antidote," by V. K. Chesnut. After a critical discussion of the work of La Cerda, Antal, Schlagdenhauffen and Reeb, Moor, Wood, and others, who applied dilute solutions of the permanganate as an antidote in cases of human poisoning caused by snake bites, phosphorus, oxalic and hydrocyanic acids, coronillin, morphin and various plant alkaloids, the writer gave the results of some experiments made with the salt by Dr. E. V. Wilcox and himself in cases of the poisoning of sheep from eating plants. These experiments were made in Montana where hundreds of sheep are killed by certain poisonous plants every year. Preliminary experiments indicate that 1 per cent. solution of potassium permanganate, to which 1 per cent. of aluminum sulphate is added, is a wholly satisfactory antidote for poisoning by two of the most poisonous groups of plants of that state, the species of death camas, *Zygadenus* spp. and the larkspurs, providing, of course, that it be given in the earlier stages of the poisoning. The aluminum sulphate was added because of the greater oxidizing value which it confers upon the permanganate. The use of the mixed salts in cases of poisoning by other plants is to be further investigated.

L. S. MUNSON, *Secretary*.

NEW YORK SECTION.

The regular meeting of the New York Section of the American Chemical Society was held on Friday evening, April 5th, at the the Chemists' Club, 108 West Fifty-fifth street, and over fifty members were present.

The following papers were read : "The Detection of Methyl Alcohol," by F. A. Sieker. "The Synthesis of Alkyl Ketodi-

hydroquinazolins from Anthranilic Acid,'' by A. H. Gotthelf. ''Note on the Determination of Moisture in Coal,'' by Durand Woodman. ''Comparison of Methods for the Electrolytic Precipitation of Iron,'' by E. F. Kern. ''The Electrolytic Precipitation of Nickel and Cobalt from a Double Cyanide Solution,'' by E. F. Kern.

In the discussion of Mr. Sieker's paper, Dr. Eccles suggested that for a method of detecting methyl alcohol depending on the production of a specific odor, he thought that which produced methyl salicylate was to be preferred as more characteristic than the one described producing formaldehyde.

Dr. Woodman's paper was an effort to ascertain more clearly the effect of oxidation in drying samples of coal according to the accepted method for determination of moisture. It appeared that the apparent loss of moisture in a stream of dry carbonic acid gas, was uniformly less than when the coal was heated in contact with the air.

This would appear to indicate that by the ordinary method there is a loss by oxidation in the first stages of heating, before the well-known increase of weight begins, by more prolonged heating.

The paper evoked considerable discussion as to whether the secondary increase of weight was due to oxidation, occlusion, or some change not yet explained. It was stated that further work was in progress with a view to clearing up some of these points.

Mr. Kern gave a very full and valuable exposition of the electrolytic methods for precipitation of iron, nickel, and cobalt.

The secretary announced that the ladies of the Society and their friends, as well as the wives of members and friends, were expected at the banquet in commemoration of the twenty-fifth anniversary of the founding of the Society, as well as at all the meetings to be held in conjunction therewith.

The chairman stated that responses to the notices of the celebration had been more numerous than for any previous meeting, and a large attendance was anticipated.

DURAND WOODMAN, *Secretary*.

OBITUARY.

PROFESSOR RACHEL LLOYD, PH.D., ZURICH.

Professor Rachel Lloyd was born at Flushing, Ohio, January 26, 1839. She died at Beverly, N. J., May 7, 1900. She was united in marriage to Mr. Franklin Lloyd, chemist with Messrs. Powers & Weightman, May 11, 1859. After the death of her husband, October 6, 1865, she spent several years abroad for her health. On returning home she was forced, by loss of property, to engage in teaching. In the private school for young ladies of Misses Bonney and Delaye, she became interested in science, and in 1876 attended the summer school of instruction in chemistry at Harvard University, which she continued to attend until 1884. As she extended her knowledge of chemistry she was promoted from one position to another, until she determined to devote her energies exclusively to chemistry. On finding that the only obstacle to her promotion to a professorship of chemistry was the fact that she had never received a degree, she resigned a good position in Louisville, Ky., and went to the University at Zurich, Switzerland, then the only place in the world where a woman could receive the doctorate degree. In two years she received the degree of doctor of philosophy with honor, and soon afterward was elected professor of analytical chemistry in the University of Nebraska, which position she held until she was forced to resign on account of failing health.

Dr. Lloyd possessed remarkable energy and force of character, combined with broad culture and great mental ability. To natural refinement and a sympathetic nature she united the culture of the best society and extended foreign travel. These qualifications with a strong and attractive personality, and the power of making personal friends of students, rendered her teaching very effective. In an address to the students of the University of Nebraska after her death, on the value of her service to the University, Acting Chancellor Bessey said : " She was not only an eminent chemist, she was a great teacher, and more than that, she was the beloved advisor and counselor of students."

Professor Lloyd's contributions to science include the following publications, with C. F. Mabery : "On Diiodbromacrylic and Chlorobromacrylic Acids ;" "On Dibromiodacrylic and Chlor-

bromiodacrylic Acids." These papers were published in the *Proceedings of the American Academy of Arts and Sciences*, and in the *American Chemical Journal*.

Inaugural dissertation for the degree of doctor of philosophy : " On the Conversion of Some of the Homologues of Benzol Phenol Into Primary and Secondary Amines. This paper was published in the *Berichte*, **22**, 491, and in *University Studies*, University of Nebraska.

Outside of her eminent work as a teacher, Dr. Lloyd's greatest work at Lincoln was in laying the foundation for the enormous development of the beet-sugar industry in the state of Nebraska. While in Switzerland, she became interested in the cultivation of the sugar-beet, and seeing the great possibilities in its extension in Nebraska, she started and directed the first experimental work. The rapid extension of this industry was due to the combined efforts of herself and Professor Nicholson.

While it is an incentive to the best endeavor to contemplate the rich fruitage of such a life, there is a feeling of sadness that the great temptation to intense effort should result in the early death of so many eminent workers.

C. F. MABERY.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Dewey, Elbert E., 518 Washington Boulevard, Chicago, Ill.
Goodmar, Julian H., 121 E. 23d St., N. Y. City.
Hyman, Leonard W., 342 S. Pearl St., Albany, N. Y.
Reckhart, D. W., Box 88, El Paso, Texas.
Stalnaker, Edwards Stuart, Thomas, W. Va.
Strange, William Wallace, Oberlin, O.
Terry, H. Warren, Jr., 2029 Mt. Vernon St., Philadelphia, Pa.
Turner, Herbert S., Oglesby, La Salle Co., Ill.
Watson, Charles A., Raleigh, N. C.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Flanders, F. F., Pullman, Wash.
Reid, Burton, 1103 W. 40th St., Kansas City, Mo.
Young, E. H., Pullman, Wash.

NEW MEMBERS ELECTED MAY 35, 1901.

Arndt, Frederick J. P., 226 E. 35th St., N. Y. City.
Breidenbaugh, Edward S., Penna. College, Gettysburg, Pa.
Broshears, John W., 27–34 Rialto Building, Chicago, Ill.
Clement, D. H., Butte, Mont.
Clevenger, Galen H., Rapid City, S. D.
Dreyfus, William, 208 E. 52d St., N. Y. City.
Friedburg, L. H., 292 VanBuren St., Brooklyn, N. Y.
Gass, James K., 717 Spruce St., Philadelphia, Pa.
Goldsmith, B. B., 19 E. 74th St., N. Y. City.
Harvey, Edward F., St. Johns, Newfoundland.
Hopkins, B. Smith, 358 W. 118th St., N. Y. City.
Krebs, August S., Del. Chem. Co., Wilmington, Del.
Rauchfuss, Eugene J., 161 E. Broadway, N. Y. City.
Ronan, Gerald P., Butte, Mont.
Ryan, Irenaeus, Barbar Asphalt Co., Long Island City, N. Y.
Schultz, Carl R., 440 First Ave., N. Y. City.
Sickels, Ivin, 17 Lexington Ave., N. Y. City.

Sims, Arthur A., Univ. of Nebr., Lincoln, Nebr.
Stevenson, M. R., Tyrone, Pa.
Thies, E. E., 125 Park Ave., Hoboken, N. J.
Thompson, Gustav W., Adams and Water Sts., Brooklyn, N.Y.
Timme, Walter, 102 W. 85th St., N. Y. City.

ASSOCIATES ELECTED MAY 23, 1901.

Davis, R. O. E., Chapel Hill, N. C.
Klugh, B. G., Chapel Hill, N. C.
Miller, Raymond M., 152 E. 20th St., N. Y. City.
Palmenburg, Oscar W., 107 W. 70th St., N. Y. City.
Rand, Charles L., 929 Lafayette Ave., Brooklyn, N. Y.
Rindskopf, Herbert A., 701 Madison St., Brooklyn, N. Y.
Shipman, William W., 20 Second St., West Manchester, N. H.
Steinmuller, William, Mineral Point Zinc Co., Mineral Point,
Wis.
Strahorn, Arthur T., Univ. of Nebr., Lincoln, Nebr.

CHANGES OF ADDRESS.

•Arnott, G. W. Campbell, Confederation Life Bldg, Toronto,
Canada.
Austen, Peter T., 80 Broad St., N. Y. City.
Bailey, Ralph W., 65 Columbia Heights, Brooklyn, N. Y.
Barnard, H. E., State Lab. of Hygiene, Concord, N. H.
Barton, G. E., care Whitall Tatum Co., Lower Works, Mill-
ville, N. J.
Bosart, Louis W., Jr., care Mrs. E. M. Durfee, 316 E. 60th
St., Chicago, Ill.
Bragg, E. B., 1116 Michigan Ave., Evanston, Ill.
Brown, H. F., Parlin, N. J.
Burleigh, W. F., care The Murphy Varnish Co., Newark, N. J.
Burnside, C. F., Parlin, N. J.
Burtt, Stratford, care Rev. Jones, 230 Classon Ave., Brooklyn,
N. Y.
Case, Wm. A., Laurel, Prince George Co., Md.
Comey, A. M., 32 Hawley St., Boston, Mass.
Dodge, Francis D., 360 Washington Ave., Brooklyn, N. Y.
Fischer, Louis A., 923 Massachusetts Ave., Washington, D. C.
Fisher, Henry, 57 E. 83d St., N. Y. City.
Fite, C. C., 102 W. 93d St., N. Y. City.
Fuller, George F., 100 William St., N. Y. City.
Given, Arthur, 1114 11th St., N. W., Washington, D. C.
Goodell, Geo. A., Mirror Lake, N. H.
Grainger, Wm. E., Box 48, Middlesborough, Ky.
Haigh, Frederic, 660 E. 23d St., Paterson, N. J.
Hardenburgh, Louis M., Hurley, Wis.
Harrison, J. B., Gov. Lab., Georgetown, Demerara, British
Guiana.

Hicks, E. F., 361 W. 27th St., N. Y. City.

Hillyer, W. E., Ches. & Pot. Tel. Co., St. Paul St., Baltimore, Md.

Hinckley, J. F., 82 Washington St., N. Y. City.

Hulett, Geo. A., 1218 S. University Ave., Ann Arbor, Mich.

Jackson, D. D., 177 Sixth Ave., Brooklyn, N. Y.

Jameson, A. H., care Cornell & Andrews, 23 Mathewson St., Providence, R. I.

Lanning, John G., Miles, O.

Levene, P. A., 1 Madison Ave., N. Y. City.

Linton, J. H., care Fraser & Chalmers, W. 12th St. and Washtenaw Ave., Chicago, Ill.

Maury, Geo. P., 545 Liberty Ave., Pittsburg, Pa.

Moody, Herbert R., 111 Bellingham St., Chelsea, Mass.

Morgan, J. L. R., Columbia Univ., N. Y. City.

Nelson, E. K., 4311 Ellis Ave., Sta. M., Chicago, Ill.

Parker, T. J., care Gen. Chem. Co., Broad Exchange Bldg., 25 Broad St., N. Y. City.

Pemberton, Ralph, Dublin, N. H.

Pough, F. H., 28 Burling Slip, N. Y. City.

Reese, C. L., care N. J. Zinc Co. of Pa., Palmerton, Carbon Co., Pa.

Reuter, L. H., 434 E. 87th St., N. Y. City.

Roscoe, Sir Henry E., 10 Bramham Gardens, London, S. W., Eng.

Schieffelin, Wm. J., 5 E. 66th St., N. Y. City.

Schniewind, F., 277 Broadway, N. Y. City.

Schoonmaker, H., care La Democrata Mine, La Cananea, Sonora, Mex.

Smith, F. Warren, care Cal. Powder Works, Los Gatos, Santa Clara Co., Cal.

Sovereign, Clarence L., Rockford, Ill.

Sticht, G. A. H., 109 Pulaski St., Brooklyn, N. Y.

Terne, Bruno, The Union Abattoir Co., Baltimore, Md.

Uhlig, E. C., 46 to 48 Barclay St., N. Y. City.

von Isakovics, Alois, care Herbene Pharmacal Co., 449 and 451 E. 121st St., N. Y. City.

Weber, Everhard, 860 Rockdale Ave., Avondale, Cincinnati, O.

Weed, Henry T., 80 Livingston St., Brooklyn, N. Y.

Welt, Ida, 128 E. 61st St., N. Y. City.

Williams, C. B., N. C. Dept. of Agr., Raleigh, N. C.

Wilson, H. T., Buena Vista, Va.

Wilson, E. F., 224 S. 8th St., Philadelphia, Pa.

Yocum, John H., Academy and Norfolk Sts., Newark, N. J.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The seventeenth meeting of the Philadelphia Section was called to order in the Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., January 17, 1901. Dr. Jayne was in the chair, and fifteen members and visitors were present.

The minutes of the previous meeting were read and approved.

Dr. John Marshall presented a preliminary note on the action of hydrogen peroxide in cleansing wounds and destroying pus, in which he showed that the gas given off was not carbon dioxide, as generally supposed, but oxygen.

A general discussion of the inaccuracies of thermometers and other chemical instruments followed, participated in by Messrs. Jayne, Taggart, Jones, Torrey, McMichael, and others.

There being no further business, the meeting adjourned at 10 P.M.

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The eighteenth meeting was called to order in the Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., February 21, 1901. Dr. Jayne was in the chair and thirty members and visitors were present.

The minutes of the previous meeting were read and approved.

The secretary announced the lecture of Prof. F. W. Clarke, at the Franklin Institute, and that the members would receive a notice.

The paper of the evening was " The Manufacture of Varnishes," by Prof. A. H. Sabin, of New York.

The paper was discussed by Drs. Jayne, Job, and others.

There being no further business, the meeting adjourned at 10 P.M. ———

The nineteenth meeting was called to order in Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., March 21, 1901. Dr. Jayne was in the chair, and twenty members and visitors were present.

The minutes of the previous meeting were read and approved.

Dr. Jayne called attention to the fact that there should be a committee on nominations.

Dr. Leffmann moved that a committee of three be appointed to prepare a list of names for nomination, to be presented at the April meeting. The motion was seconded and carried.

The paper of the evening was "Some Recent Developments in Synthetic Indigo," by J. Merritt Matthews.

The paper was discussed by Drs. Jayne, Leffmann, and others.

There being no further business, the meeting adjourned at 9.45 P.M.   F. E. DODGE, *Secretary.*

WASHINGTON SECTION.

The 126th regular meeting was held April 11, 1901, when the following program was presented :

" A New Method for the Estimation of Cane-sugar in Presence of Lactose," by L. M. Tolman.

Benzoic sulphinide was used as the hydrolyzing agent, because it has no action on the rotation of lactose, even after heating for several hours, while a solution of sucrose is completely inverted in thirty minutes by use of 0.5 gram of the sulphinide. The results obtained showed that it was a satisfactory and accurate method.

The method used in condensed milk was as follows :

Twice the normal weight of the milk was weighed into a 200 cc. flask and 10 cc. of a 10 per cent. solution of citric acid added to coagulate the casein. The liquor was then filtered, 75 cc. of the filtrate measured into a 100 cc. flask, 0.5 gram of saccharin added and after shaking, in order to break up the lumps, immersed in a boiling water-bath for thirty minutes. Two cc. of acid mercuric nitrate were then added, the solution made up to volume, filtered and polarized at as near 20° C. as possible. The direct reading was taken in the ordinary way and the volume of precipitate corrected for by double dilution. The results obtained were very satisfactory.

" Classification of Alkali Soils," by Frank K. Cameron.

The views presented in this paper may be summarized as follows :

(1) A classification as black alkali or white alkali, depending upon the presence or absence of sodium carbonate, is inadequate in view of our present knowledge of alkali phenomena. A more comprehensive classification is desirable. Such a classification appears to be possible on chemical grounds, considering alkali conditions as the result of the action of aqueous solutions of certain soluble salts upon less soluble salts.

(2) The action of sodium chloride solutions upon gypsum is the predominating feature in certain areas, and seems to be well typified by the conditions in the valley of the Pecos in New Mexico. The solubility of the gypsum is apparently much increased by the presence of the sodium chloride, due to the formation of the soluble salts, sodium sulphate and calcium chloride.

In such an area, practically the only salts which will have to be considered in the ground solutions are sodium chloride and sodium sulphate, as well as calcium sulphate. Calcium chloride is sometimes found concentrated to a considerable extent, but usually in localized and generally small spots. Owing to its keeping the soil of these spots moister and, therefore, darker than the surrounding soils, such spots are locally known as black alkali spots.

(3) The action of solutions of sodium chloride upon calcium carbonate is the predominating feature of some areas. The region about Fresno, Cal., seems to furnish a good illustration of this class. As a result, there is always found a greater or less formation of sodium carbonate, the soluble and very noxious component of black alkali, and the very soluble calcium chloride. Such regions are generally further characterized by the presence of a hard pan at a distance of a few feet below the surface and generally parallel to it, the cementing material of which is calcium carbonate. In such areas there is a tendency toward an accumulation of the soluble carbonates at the surface of the soil. Calcium chloride accumulations, in spots of comparatively restricted area, are frequent accompaniments, and are often mistaken for bad black alkali spots, although the presence of soluble carbonates in more than very small quantities is an impossibility.

(4) The class of alkali most commonly encountered is that in which the predominating feature is the simultaneous action of solutions of sodium chloride upon gypsum and calcium carbonate. In such an area, the formation of soluble carbonates can take place to only a very limited, generally negligible, extent. The apparent increase in the solubility of the gypsum is also much less than when the calcium carbonate is not present. The alkali of the Salt Lake Valley appears to be a good illustration of this type.

(5) Much less frequently other types of alkali are encountered, as at Billings, Mont., where the soluble material in the soils appears to be almost entirely sulphates.

(6) Modifications of the types described above are more or less frequently found. They may possibly be of such importance as to warrant a separate classification, as, for example, the conditions found to exist in the valley of the Sevier, Utah.

(7) The classification here proposed is believed to be comprehensive and is founded on scientific principles. It is elastic and will readily admit of modifications. Principles other than those now recognized in it may be introduced without the accompaniment of radical changes. It can be made as specific as the advance of our knowledge from time to time will justify.

"Chemical Examination of Alkali Soils," by Atherton Seidell.

In this paper the author pointed out the necessity for uniform methods in the examination of the water-soluble compounds of alkali soils, in order that the work of various investigators may

be compared. A description of the procedure and methods in use in the U. S. Department of Agriculture was given, with a full discussion of the basis therefor The unique features are the preparation of the solution for analysis, the preliminary determination of the salt content by means of the electrolytic bridge, and the determination of carbonates, bicarbonates, and chlorides. The statement of the results was also discussed at length.

An adjourned meeting was held in Hopkins Hall, Johns Hopkins University, Baltimore, Md., on April 27th, when the following program was presented :

"The Lowering of the Freezing-Point of Aqueous Hydrogen Dioxide," by H. C. Jones.

The author stated that an attempt was made to measure the dissociating power of hydrogen dioxide by means of the conductivity method. This method was abandoned since all the metals used as electrodes decomposed the dioxides, even at zero degrees. The lowering of the freezing-point of aqueous hydrogen dioxide by certain salts was measured and was found to be less than the lowering of the freezing-point of water under the same conditions.

"The Preparation of Semipermeable Membranes for the Demonstration of Osmotic Pressure." by Prof. H. N. Morse.

The author referred to the difficulties encountered in the preparation of osmotic cells by the method of Pfeffer and stated the results of some preliminary experiments, undertaken in co operation with Dr. D. W. Horn, in attempting to overcome these difficulties. Instead of expelling the air from the walls of the cups by immersion in water and exhaustion with an air-pump, as is done in the method of Pfeffer, electrical endosmose was employed, the cup being immersed nearly to the top and filled with a dilute solution of potassium sulphate, then surrounded by a cylindrical electrode and another one placed inside. A one-ampere current was passed through the solution for fifteen minutes, from the outer to the inner electrode, causing a rapid passage of liquid through the walls of the cup and freeing them from air. The cup was then removed, emptied, rinsed and placed in water until used for the formation of membrane. The method described by the author was as follows :

A cup whose walls had been freed from air and filled with water was placed in a solution of a copper salt and filled with a solution of ferrocyanide. A current was passed from the outside inward, the copper and ferrocyanogen ions being driven into the walls from opposite directions; a membrane was built up wherever they met. The results were very satisfactory. The method of construction of the electrodes was described, and the

resistance of the cups stated. On breaking the cup, the membrane was found as a reddish brown line, usually in the middle of the wall, though deviating more or less to one side or the other.

" Molecular Rearrangement of Sulphamine Acids," by Dr. Ira Remsen.

"On a Reduction Process for Tin at Comparatively Low Temperatures, and Recovery from Waste Products," by Chas. Glaser.

This paper gave a description of a process patented by John C. Toliaferro for the recovery of tin from waste products. The refuse from tin-plate works consists of the remnants of the fatty acids used to protect the black plates from reoxidation after cleaning with acid, and more or less oxidized tin, which often contains some free metal or mixed oxides of tin and lead. The refuse from the oils often contains oxides of the two metals, which are usually recovered by burning off the oil and collecting the residue and metallic fumes. The united dross is reduced to metal in a suitable furnace. Mr. Toliaferro observed that under certain conditions he obtained metallic tin from the refuse fatty acids by heating them to incipient decomposition. Certain experiments were made, showing that at a temperature a little above the melting-point of tin, stannous soaps are reduced to metallic tin, gaseous products, and some carbon. From these observations, the following reduction process was evolved :

A large iron pot is heated from below, so that a piece of tin dropped at the bottom will melt. The pot is then filled with refuse fatty acids and the heat increased until they commence to give off vapors. Stannic dross is then introduced with stirring. This may be continued at pleasure, or until the fatty acid is almost used up. The reduced tin is removed at convenient intervals.

"On Dr. Theodore Meyer's Tangent System of Sulphuric Acid Chambers," by Chas. Glaser.

The author described a modification of the construction and working of lead chambers used in the manufacture of sulphuric acid. The modification relates to the shape of the chambers and the motion of the gases. Ordinarily the chambers are square and the gases introduced in such a way that they traverse the chambers but once, get only moderate mixing, except where they fall upon the chamber curtains and where they are forced through relatively narrow connecting pipes between chambers. In the modification described, the chambers are round or polygonal, the gases are introduced near the ceiling in the direction of a tangent and are removed through the center of the bottom by suitably constructed pipes. Experiments show that the gases move first

along the sides of the chamber, drifting towards the center in such a way that the whole content gets into rotation. Cooling and draught bring the whirpool in the center to the exit pipe. When introduced into the second chamber the gases retain the revolving motion derived from the first to which is added the motion of the second so that an epicycloid motion is produced. The gases traverse the chambers a good many times, increasing largely the amount of work performed. It has been demonstrated that by this method the necessary chamber space for one pound of sulphur in twenty-four hours is reduced to below 10 cubic feet as against 20 in the old system. The author stated that the cost of producing sulphuric acid, so far as labor and lead chambers are concerned, is reduced to 50 per cent. of what it was by the old method.

" The Solubility of Gypsum in Aqueous Solution of Certain Electrolytes," by Frank K. Cameron and Atherton Seidell.

This paper gave a description of the complete solubility curves for gypsum in aqueous solutions of sodium chloride, magnesium chloride, calcium chloride, sodium sulphate and a mixture of sodium chloride and calcium hydrogen carbonate at $25°$ C. With sodium chloride and magnesium chloride the curves show maximum points. The formation of complex ions, the authors believe to be possible and probable, but the deviations from the *mass law* are more likely to be due to a condensation of the solvent itself.

With sodium sulphate it was shown that the solubility of the gypsum first decreased and then increased, with increasing concentration of the more soluble salt, until it became greater than in pure water. It is believed that a double salt was formed in the solutions, possibly identical with the mineral glauberite. It did not separate from the solutions on evaporation, however, at ordinary temperatures. Here again the authors think the condensation of the solvent probably plays an important rôle and, under such circumstances, it is probable that the sodium sulphate dissociates to a large extent or completely as a di-ionic electrolyte. The composition of the solid phase, containing both calcium sulphate and sodium sulphate, did not apparently affect the composition of the solution in contact with it. This is regarded as of sufficient interest to merit further investigation. In solutions of calcium chloride the solubility of the gypsum decreases quite rapidly at first and then very slowly but steadily as the concentration of the more soluble salt increases.

When calcium carbonate in the solid phase was also in contact with solutions of sodium chloride, and was brought to equilibrium with ordinary air, it was found that up to the concentrations of about 80 grams per liter of sodium chloride, the gypsum dissolved in very nearly the same quantities as though

the calcium carbonate were not present. From this point on, however, the curve makes a sudden drop, and then the solubility of the gypsum slowly decreases.

Applications of the results to geological and technical studies were indicated, and a theoretical discussion accompanied the description of the experiments.

"The Solubility of Calcium Carbonate in Aqueous Solutions of Certain Electrolytes and in Equilibrium with Air," by Frank K. Cameron and Atherton Seidell.

Since the solubility of the calcium carbonate is dependent upon the amount of carbon dioxide in the gas phase in contact with the solution, the solutions were brought to equilibrium with air, previously washed in dilute sulphuric acid, and bubbled through the solutions by means of an aspirator. It was found that the curve for sodium chloride presented a well-marked maximum point. No normal carbonates were in the solution, the calcium dissolving entirely as the hydrogen carbonate.

In sodium sulphate solutions, the major part of the calcium dissolved as the hydrogen carbonate, though at the higher concentrations normal carbonates were also found. The curve for this pair of electrolytes showed no maximum point. Curiously, it was found that calcium carbonate was much more soluble in solutions of sodium sulphate than in solutions of sodium chloride at all concentrations.

The presence of solid gypsum was found to produce an effect on the solubility of calcium carbonate in sodium chloride solutions, greater in amount, but similar in nature to that produced by calcium carbonate on the solubility of the gypsum in sodium chloride solutions, and described in the preceding paper. Practical applications of the work were pointed out, and a theoretical discussion of the results obtained was given.

L. S. MUNSON, *Secretary.*

CHICAGO SECTION.

A meeting of the Chicago Section was held at the Sherman House, Wednesday evening, April 10, 1901.

After the usual dinner, Dr. Jacques Loeb, of the University of Chicago, gave a paper on the "Physiological Action of the Ions." This dealt chiefly with the effect of certain salts, especially those of calcium and potassium on the fertilization of sea-urchin eggs.

F. B. DAINS, *Secretary.*

NORTH CAROLINA SECTION.

The regular meeting of the North Carolina Section of the American Chemical Society was held in the State Chemist's

office, Agricultural Building, Raleigh, on April 27, 1901, at 11 A.M., with Prof. Kilgore in the chair. Twenty-seven members and visitors were present.

The annual election of officers for the ensuing year were:

W. A. Withers, President; W. J. Martin, Jr., Vice-President; C. B. Williams, Secretary-Treasurer; Charles Baskerville, Representative in Council of the American Chemical Society; Executive Committee, W. A. Withers, W. J. Martin, Jr., and C. B. Williams.

The following program was presented and discussed:

"Basis of Scientific Thought," by Charles Baskerville.

"The Chemical Composition of Cotton-Seed Meal," by W. A. Withers and G. S. Fraps.

The authors found that the average amount of betaïn and cholin in seven samples of cottonseed meal was 0.28 per cent., the ratios being (the average of two samples) betaïn : cholin : : 78.5 : 21.5.

Gossypein, if present, is in minute quantity. Of the nitrogen-free extract, 29.2 is pentosans, and 47.4 per cent. raffinose. The pentosans of the meal were found to be insoluble in diastase, and were contained entirely in the nitrogen-free extract, unless an unusually large amount of hulls was present.

Cottonseed meal contains no starch, and inappreciable quantities of sucrose and of reducing sugars. The average of five samples gave organic acids 0.48 per cent.

"The Recent Advances in Physiological Chemistry," by A. S. Wheeler.

"Alcohol as An Antidote for Carbolic Acid," by E. V. Howell.

(1) In this paper attention was called to the fact that experiments upon the author, beginning early in 1899, show that alcohol removes the escharotic effect of carbolic acid on the arm and in the mouth.

(3) That on account of the alarming increase in its use for suicidal purposes, and the large number of accidents because of its general use as a disinfectant, carbolic acid should be scheduled as a poison in the poison laws of the various states and its sale restricted.

(3) That alcohol is on record as an antidote and the results demand a thorough investigation. It must act most probably in one of three ways: (a) As a simple addition to counteracting the escharotic effect; (b) as a chemical antidote, forming an inactive or less active compound; (c) as a physiological antagonistic, its stimulating effect combatting the depressant effect of the phenol.

In investigations being carried on, so far no chemical reaction between carbolic acid and alcohol, or carbolic acid and camphor (which also removes the escharotic effect) has been observed.

. "The Presence and Detection of Arsenic in Beer," by W. Grimes Haywood.

This paper was a review of the recent cases of poisoning in England, due to the presence of arsenic in beer, and a comparison of the methods for the determination of that element.

"A New Meteoric Iron from Davidson County, North Carolina," by Joseph Hyde Pratt.

This iron was found on a hillside, rising just east of Lexington—Troy road, about half mile south of Cid P. O., Davidson County. The iron originally weighed 13 pounds, 14 ounces, and was somewhat oblong in shape, and its surface is more or less pitted. Testing the polished surface failed to reveal either the Widemann-stattian figures or the Neumann lines ; but the etched surface presents a granular or stippled appearance overlain with a network of fine lines, and the fractured surface shows traces of what is apparently an octahedral cleavage. This etched surface, while being different from other meteorites, is also different from any of the manufactured irons that have been tested.

An analysis by Dr. Baskerville gave : Iron, 93.89 ; manganese, 0.92 ; nickel, 0.30 ; cobalt, 0.34 ; silicon, 0.62 ; carbon, 3.88 ; but sulphur, phosphorus, titanium, aluminum, and copper were absent. Dr. Pratt claims that the presence of nickel and cobalt and the absence of sulphur, phosphorus, etc., together with its structure and more or less isolated country in which it was found, lead to the belief that this iron is of meteoric origin. The name proposed for it is the Cid Iron.

"Ulsch–Street Method Modified to Include Organic Nitrogen in Samples Containing Nitrates and Chlorides," by W. M. Allen.

The author recommends the following :

Place 0.7 gram sample in a 250 cc. Kjeldahl digesting flask. Add about 1 gram of reduced iron, 30 cc. water, and 10 cc. dilute sulphuric acid (1 to 1). Shake well and let stand fifteen or twenty minutes. Heat slowly so that solution will boil gently for ten or fifteen minutes, then briskly until two-thirds of water has boiled off. Cool slightly, add 25 cc. sulphuric acid and 0.7 gram mercuric oxide. Digest and distil as in the Kjeldahl method. In samples of pure nitrate, add 0.5 gram of ferric chloride to the water to dissolve first nitric oxide set free, and digest only for the nitric nitrogen. The presence of a large amount of iron salts must be guarded against, or else violent bumping will give trouble in distillation.

"The Nature of Pentosoids and Their Determination," by G. S. Fraps.

The author divides pentosoids into water-soluble, acid-soluble, soluble in cold caustic soda solution ("wood gum") and difficultly soluble. Members of the first three classes have been hydrolyzed to pentose, and are called pentosans. The last class includes lignocelluloses, oxycelluloses, etc., and have not been hydrolyzed to pentoses. The crude furfural from vegetable materials obtained in the pentosan determination was found to contain a body which is precipitated by phloroglucinol and destroyed by distillation with hydrochloric acid. Its occurrence, distribution, and digestibility were discussed as well as the effect of its presence on the pentosan determination.

"An Automatic Filter-Washer," by J. M. Pickel.

This apparatus consists of (1) a reservoir for water with which to wash; (2) a rubber tube, provided with thumb-screw clamps, leading from the reservoir to the (3) delivery vessel which, by means of a small siphon, delivers the water intermittently on the filter; (4) a funnel containing the filter, and set in this funnel, a smaller inverted funnel; (5) means for disposing of the washings. When once set going, the apparatus needs no further attention, and is especially applicable in determining water-soluble nitrogen in fertilizers and also water-soluble phosphoric acid (although not yet in use for this latter purpose).

"Note on the Latent Heat of Vaporization of Liquids," by J. E. Mills.

"Note on the Determination of Insoluble Phosphoric Acid," by C. D. Harris.

Mr. Harris exhibited an arrangement which had proved, in his hands, very satisfactory in filtering and washing citrate-insoluble phosphoric acid. He substitutes a carbon filter, in the bottom of which is a porcelain disk covered with asbestos for the slow and hazardous method of using a funnel and hardened filter-paper.

"Contribution to the Chemistry of Thorium; Evidence Pointing to the Existence of a New Element, 'Carolinium,'" by Chas. Baskerville.

The author has obtained thorium salts from five different sources and purified them. By the action of sulphur dioxide on the neutral chlorides and by fractioning the citrates, oxides are eventually obtained which indicate the complexity of thorium. The pure oxide has a specific gravity of 9.8 according to some authorities and 10.2 according to others. The purified oxide mentioned had a specific gravity of 10.1; after fractioning, one had a specific gravity of 9.4 and the other 10.57; intermediate fractions gave 9.6 and 10.4. Although atomic weight determinations have not been made, there is much evidence in favor of the existence of a new element, which the author would name "Carolinium."

To avoid criticism the author stated his excuse for presenting the paper before the work was completed. Having made these observations quite four years ago, in the *interim* he has been engaged in securing direct from monazite sufficient quantity of pure thorium salts. Five thousand liters of solution have been worked up. The author's supply of the element has been much augmented through the kindness of Dr. Waldron Shapleigh, of the Welsbach Light Company, who presented him with two kilograms of his purest thorium oxalate. Last fall the author wrote Professor Bohnslar Brauner, of Prague, who had made the most recent atomic weight determinations of thorium about his experiments. Not hearing from Dr. Brauner, the author was surprised to see in the *Proceedings of the London Chemical Society*, April 10, 1901, an article on "Contributions to the Chemistry of Thorium," by Dr. Brauner, in which he states that he had fractioned thorium by hydrolysis of the oxalate into two bodies which he termed Thα and Thβ. Brauner's work, as reported, was by no means complete. While the author insists that he holds the very highest opinion of Professor Brauner, and while neither his work nor the motives prompting Professor Brauner in making this preliminary publication are called into question, in justice of the author's work along these lines, it was not deemed unscientific to present the results of incomplete observations.

"The Systematic Investigation of Soils," by B. W. Kilgore.

After the transaction of some miscellaneous business, the Section adjourned to meet in the summer.

C. B. W..LIAMS, *Secretary*.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Aspinwall, Henry C., Pompton Lakes, N. J.
Bjèrregaard, August P., Debevoise Ave., cor. Bullion St., Brooklyn, N. Y.
Hemwood, Abraham, Drexel Inst., Philadelphia, Pa.
Larcar, H. C., Deoghur, Baidyanath, India.
Reynolds, Albert A., Williamstown, Mass.

NEW MEMBERS ELECTED JUNE 6, 1901.

Falding, Frederic J., Exchange Court, 52 Broadway, N. Y. City.
Frusher, Tom, 87 Nassau St., N. Y. City.
Fudge, Thomas, 43 W. 27th St., Bayonne, N. J.
Fuerst, W. F., 2 Stone St., N. Y. City.
Gordon, Frederick T., Navy Yard, Philadelphia, Pa.
Johnson, Thomas H., 28 Hinchman St., Dover, N. J.
Lewis, W. B., care Sargent Co., Chicago Heights, Ill.
Lyons, Albert B., 72 Brainard St., Detroit, Mich.
Mark, Kenneth L., 109 Irving St., Cambridge, Mass.
Mosesom, Morris, 1813 Lexington Ave., N. Y. City.
Novarine, John L., 101 Henry St., Brooklyn, N. Y.
Stoddart, Charles W., 526 S. Broadway, Yonkers, N. Y.
Tiemann, Hugh P., 125 W. 43rd St., N Y. City.
von der Linde, Harold T. G., 101 Tyndall Ave., Toronto, Canada.
Wirth, Adam, 1004 Aline St., New Orleans, La.

ASSOCIATES ELECTED JUNE 6, 1901.

Marsh, L. Stanley, Ann Arbor, Mich.
Saxe, Sigmond, 108 Fulton St., N. Y. City.
Silverman, Alexander, Western Univ., Allegheny, Pa.

CHANGES OF ADDRESS.

Archibald, E. H., Harmony, Colchester Co., N. S.
Bizzell, J. A., Dunn, N. C.

Cary, Edward A., 66 Clinton Ave., Montclair, N. J.
Cushman, Allerton S., Pomfret Centre, Conn.
Davis, R. O. E., Chester, S. C.
Fowler, R. E., Wauwatosa, Wis.
Gascoyne, W. J., 23 South St., Baltimore, Md.
Grayson, William, Jr., 1115 South Grand Ave., St. Louis, Mo.
Heileman, W. H., Elwell, Iowa.
Kendall, Arthur J., Expt. Station, Lawrence, Mass.
Logan, Miss Lily, Howardsville, Va.
Nichols, W. H., Broad-Exchange Bldg., 25 Broad St., N. Y.
City.
Reese, Herbert J., Livingston, Mont.
Reid, E. Emmet, Baylor Univ., Waco, Texas.
Root, Wm. L., 11 Church St., Pittsfield, Mass.
Voorhees, S. S., care Supt. Architect, Treasury Dept., Washington, D. C.
Vreeland, C. D., Upper Montclair, N. J.
Weston, David B., Sharon, Mass.
Wolfe, J. V., Jr., Alma, Mich.
Youtz, L. A., Middlefield, Mass.

MEETINGS OF THE SECTIONS.

NEW YORK SECTION.

The May meeting of the New York Section was held at the Chemists' Club, May 10th; it was called to order at 8.20, P.M., 55 members present and Dr. C. A. Doremus presiding. The minutes of the previous meeting were omitted, owing to the absence of the secretary.

The reading of papers was in the following order : "The Quantitative Determination of Cadmium," by E. H. Miller and R. W. Page ; "On the Relation of the Chemical Constitution to the Physiological Action of Certain Modern Anesthetics," by W. E. Dreyfus ; "Alloys of Titanium and Titanium Steel," by A. J. Rossi ; "The Chemical Nature of the Enzymes," by P. A. Levene (read by Dr. S. Bookman) ; "Note on Nucleic Acid," by P. A. Levene (read by Dr. S. Bookman) ; "Analysis of Garden Sage, with Notes on the Determination of Essential Oils," by L. L. Watters.

Each of the papers received some discussion.

A communication was read from Mr. Clifford Richardson, chairman of the New York Section of the Society of Chemical Industry, relative to the appointment by that body of a committee to secure "Uniformity in Technical Analysis," and stating that a sub-

committee had been appointed to investigate the subject of the analysis of Portland cement; also, that work on this line had already been entered into, and that members of the New York Section were invited to cooperate.

Prof. Bogert moved that the New York Section bring this action of the New York Section of the Society of Chemical Industry to the attention of the council and recommend that a committee be appointed to cooperate with the committee from the Society of Chemical Industry. The motion was duly seconded and carried.

Prof. Bogert moved that hereafter the chairman of the New York Section be returned as a local delegate to the council of the Society, provided he be not already a member of the council as delegate at large. The motion was seconded and carried.

The chairman announced that the June meeting would be one for the election of officers. The meeting adjourned at 10 P.M.

(From record by the chairman.)
DURAND WOODMAN, *Secretary.*

The June meeting of the section was held on Friday evening, June 7, 1901, at the Chemists' Club, 108 West 55th Street. Dr. Charles A. Doremus occupied the chair, and about 50 members were present.

The minutes of the April meeting were called for, read and accepted. The minutes of the May meeting were read and accepted.

The secretary's report stated that the nine regular meetings had been held, at which twenty-nine papers had been read. No special meetings had been called.

Ninety members had been elected; eighteen have moved out of the section limits; eight have resigned; death has removed seven. The net increase in membership is, therefore, 57.

The treasurer's report showed the total expense for the year as a little over $400.00. Checks amounting to $350.00 had been received from the treasurer of the general society, and bills amounting to a little over $50 are due and unpaid.

A. P. Hallock and C. F. McKenna were appointed auditors of the treasurer's account.

The election of officers was then proceeded with as follows: Chairman, M. Taylor Bogert was unanimously elected; Vice-Chairman, Durand Woodman; Secretary-Treasurer, Messrs.

McIlhiney and Mathews, being nominated for the position of secretary-treasurer, a vote resulted in the election of J. A. Mathews by twenty-four to nine; Executive Committee, P. C. McIlhiney (Columbia), Prof. E. H. Miller (Columbia), T. C. Stearns (Jersey City); Delegates to the Scientific Alliance, Wm. McMurtrie, Prof. Marston T. Bogert, H. C. Sherman(Columbia University).

In accordance with the by-laws, the newly elected chairman and secretary were invited to at once assume their duties, each, however, declining in turn, and requesting that the presiding officers continue their services until the close of the meeting.

It was then moved and seconded that Section III of the by-laws be amended to read that " the officers shall be elected by ballot, and shall assume their duties at the close of the meeting at which they are elected."

In accordance with ruling by the chair, it was moved to lay the motion to amend on the table until the next regular meeting. The motion was seconded and carried.

It was further moved, seconded, and carried, that the secretary be requested to prepare a section book containing reports of the secretary and treasurer, a list of papers read, a list of the members of the section, giving their occupation, location, and any other matters concerning the section suitable for such publication.

Papers were read as follows : " Some Experiments with the Mononitro-orthophthalic Acids," by M. T. Bogert and L. Boroschek ; " On the Maumené Tests for Oils, by H. C. Sherman, J. L. Danziger, and L. Kohnstamm ; " On the Separation and Determination of Uranium," by E. F. Kern.

The paper on the " Maumené Tests for Oils " was a brief account of the principal results obtained in a series of experiments on several varieties of oils, with different modifications of the Maumené test. The common practice of diluting oils with petroleum to prevent too violent a reaction was found to give unsatisfactory results, the figures obtained from such mixtures being too high, as was also the case when the oil was dissolved in an equal weight of carbon bisulphide or chloroform. The necessity of taking account of the specific heats of the oils and diluents was noted. In order to avoid the necessity of diluting the oil and the resulting uncertainty in the interpretation of results, the use of a weaker acid was proposed. Sulphuric acid, of

about 87 per cent., can be added directly to all the common oils and the test can be carried out in exactly the same way for the drying as for the non-drying oils. Even when calculated as "specific temperature reaction" the results are somewhat influenced by the strength of the acid used, higher figures being obtained with the more concentrated acids. It was, therefore, recommended that the test be always made with acid of such strength as will give with water a rise of 33° to 34° C.

It was announced that the courtesies of the Society had been extended to Professor van't Hoff, and a motion was made and unanimously carried, authorizing the chairman and executive committee to take such measures and make such preparations as might be required for entertaining Professor van't Hoff.

The meeting then adjourned until October.
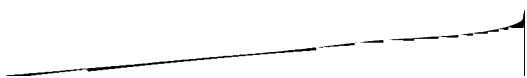
DURAND WOODMAN, *Secretary.*

CHICAGO SECTION.

A well attended meeting of the Chicago Section was held at the Sherman House, Wednesday, May 16th.

The speaker of the evening was Prof. A. Nicholson, of the University of Chicago, who gave a paper on "Some Recent Applications of Spectrum Analysis."